PATHWAYS UTILIZED BY HEAVY METAL POLLUTANTS IN URBAN STORMWATER RUNOFF

by

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A Thesis Submitted for the Degree of
DOCTOR OF PHILOSOPHY

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THE UNIVERSITY OF ASTON IN BIRMINGHAM

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SUMMARY

The research concerned the assessment of the pathways utilized by heavy metal pollutants in urban stormwater runoff. A separately sewered urban residential catchment of approximately 107 hectares in Chelmsley Wood, north-east Birmingham was the subject of the field investigation.

The catchment area, almost entirely residential, had no immediate industrial heavy metal input, however, industry was situated to the north of the catchment. The perimeter of the catchment was bounded by the M6 motorway on the northern and eastern sides and was believed to contribute to aerial deposition. Metal inputs to the ground surface were assumed to be confined to normal suburban activities, namely, aerial deposition, vehicular activity and anthropological activities.

A programme of field work was undertaken over a 12 month period, from July 1983 to July 1984. Monthly deposition rates were monitored using a network of deposit cannisters and roadside sediment and soil samples were taken. Stormwater samples were obtained for 19 separate events. All samples were analysed for iron, lead, zinc, copper, chromium, nickel and cadmium content. Rainfall was recorded on site with additional meteorological data obtained from local Meteorological Offices.

Use was made of a simple conceptual model designed for the catchment to substantiate hypotheses derived from site investigations and literature, to investigate the pathways utilized for the transportation of heavy metals throughout the catchment.

Key words: Heavy metals, Pathways, Stormwater, Deposition, Model.

This thesis is dedicated to the
memory of my dear Father

Cliff Wren

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CHAPTER 1

INTRODUCTION

The current debate on the detrimental effects of stormwater pollution loadings, especially those of heavy metals, prompted the study of this problem within a catchment in Chelmsley Wood, near Birmingham. The primary objective was to assess the heavy metal component of the pollution load within the stormwater runoff and to establish the pathways followed by the heavy metal pollutants as they entered and passed through the catchment. The long term objective was to produce a computer model of the system to assist in pollution management.

From the literature search an hypothesis was developed as to the various pathways with which metal pollutants could follow within a given catchment area. A programme of field work was then initiated. Later a simple conceptual model was designed (Hedges et al (1985)) to evaluate the hypotheses developed as a result of site investigations.

Experimental work at the Chelmsley Wood site was initiated by Birmingham City Council in 1978, in an atempt to assess the impact of stormwater pollution loadings on the receiving waters and to contribute to the debate on the adoption of separate as opposed to combined sewerage systems.

Early work at the Chelmsley Wood site has been reported by Mance (1981) and an earlier study by Smith (1979). However, since that time, little work had been carried out, apart from flow and rainfall monitoring, with the occasional analysis of stormwater samples by Birmingham City Council, until the present research project.

The experimental catchment was part of an estate constructed between 1965 and 1969, situated approximately 17 km to the north-east of Birmingham city centre. The site was originally selected due to the presence of a completely separate sewer system and there was little chance that it had been corrupted by either direct connections of foul water drains or by seepage from them, due to its recent construction.

The characteristics of the catchment were determined from aerial photographs using remote sensing techniques. The area of Chelmsley Wood was almost entirely a residential council estate, with an estimated population of 11500 in approximately 3200 dwellings. Due to the nature of the site there was no immediate industrial heavy metal input, but industry to the north and the M6 motorway which bounded the northern and eastern sectors of the experimental catchment were believed to contribute to aerial deposition, particularly when the prevailing wind was from that quarter.

Since the site was almost entirely residential, with no direct industrial contributions it was assumed that the pollution inputs to the sewerage system were limited to normal suburban activities, aerial deposition, vehicular activity and anthropological activities.

It order to quantify these inputs and to evaluate the pathways of individual pollutants from source to sewer, it was deemed necessary to consider both landborne and airborne sources of pollution. A sampling programme was designed and later implemented to monitor the various pathways.

The programme of fieldwork was initiated in 1983. Over a twelve month period from July 1983 to July 1984, monthly aerial metal deposition rates were measured using a network of deposit cannisters. In addition road sediment samples were taken at the same locations to that of the deposit cannisters and soil samples were taken at random locations throughout the catchment.

Rainfall was recorded on site by two tipping bucket raingauges with the measurements recorded onto a data logger, the tapes of which were later deciphered by Birmingham City Council. Additional meteorological data were obtained from local meteorological offices.

Stormwater samples, flow data and other quality measurements were collected at a manhole on a 1.4 m diameter outfall sewer at a point where it left the experimental catchment. Over the study period stormwater samples were obtained for nineteen separate events, fifteen of which were studied in depth.

All samples collected were analysed for the same seven heavy metals, namely, iron, lead, zinc, copper, chromium, nickel and cadmium, by Atomic Absorption Spectrophotometry.

In order to assess vehicle activity within the catchment, a manual traffic survey was carried out. With additional information provided by the West Midlands County Council (WMCC), the data obtained were extrapolated to determine the vehicle kilometers travelled per day, during each week of the year.

Finally, records of road maintenance practices (road sweeping and gully pot cleaning) and de-icing activities for the sampling period were obtained from Solihull District Council.

In order to handle the vast amount of data acquired during the research project, a computerized data base management system (Dbase II) was used and the data were interpreted using various software packages.

The preliminary findings of the model are discussed, together with the shortcomings of the data available for its calibration. The outcome of the model indicated that the hypotheses developed concerning the pollution pathways were essentialy correct, as reasonable agreement was found between the observed and simulated events. The model was also used to obtain mass balances of metals over the twelve month period and produced monthly variations in the metals discharged to the receiving watercourse.

This thesis describes the experimental catchment and the methods of sampling and analyses used. The heavy metal deposition, road sediments, soil and stormwater analyses and the conceptual model that was employed to establish the pathways utilized by heavy metals through the catchment are described in separate Chapters. The following Chapter is concerned with an introduction to sewer systems.

CHAPTER 2

AN INTRODUCTION TO SEWER SYSTEMS

2.1 Historical Background

Sanitation works are known to have existed in ancient times and archaeologists have discovered drainage systems which were in use in Roman cities over two thousand years ago.

The earliest archaeological records for municipal water supply and wastewater disposal date back five thousand years to the city of Nippur in Sumeria (Baker (1949)), where the drains were intended, primarily, to carry away runoff from storms and the flushings of streets. From that time until the middle of the nineteenth century there were no significant changes in sewerage system design.

In the United Kingdom and other European countries there was no incentive to provide sanitation until the nineteenth century. At that point in time, with the advent of piped water supplies and the subsequent need for an effective means of removing waste waters, sewerage systems were developed (Bartlett (1970)).

Following cholera epidemics in London in 1848 and again in 1854, the connection between contaminated water supplies and the spread of the disease was made. Finally it was recognized that the absence of any effective sewerage system was a major hindrance in combatting the problem of disease and poor sanitation.

In 1855 Parliament passed an Act "for the better management of the metropolis", which provided the Metropolitan Commission of Sewers with suitable powers to enable the initiation of the construction of a sewerage system.

The obvious remedy for the foul conditions that existed was for human excrement to be discharged into the existing storm sewers, and additional collection systems to be added. This solution created the combined sewers, a feature of the older metropolitan areas. The natural purification process of receiving watercourses subsequently tended to become overtaxed as a result of the increased pollution loadings discharged from the sewers, and many were themselves then culverted and converted into sewers. However, with time the larger watercourses became increasingly polluted, with the eventual result in that need for the provision of treatment facilities was recognized.

It was not until the latter half of the nineteenth century, when attempts were made to find remedies for these pollution problems, that separate and partially separate sewerage systems were developed.

2.2 Sewerage

Sewerage is defined in the BS CP 2005 (1968) as follows:

> "a system of sewers and ancillary works to convey sewage from its point of origin to a treatment works or other place of disposal".

Sewers are designed to collect and convey both domestic and industrial waterborne wastes and surface water runoff. In the United Kingdom, most sewer systems consist of pipes laid underground in tree-like (dendritic) patterns, often incorporating an old watercourse that has been culverted.

There are two main types of sewer systems, namely, combined and separate.

2.2.1 Combined Sewer System

The combined sewer system employs a single network of pipes to carry both stormwater and sanitary sewage. During periods of dry weather flow the sanitary sewage is collected and routed to an interceptor point, where it is diverted to the sewage treatment plant. The interceptor system is designed for a capacity between one and a half to five times the normal dry weather flow. Runoff from small storms are therefore given the same treatment as sanitary sewage. However, whenever the flow in the pipes exceeds the capacity of the interceptor system the additional flow is directed to the stormwater outlet. As a result during moderate and heavy rainfall almost all of the sanitary sewage is discharged, untreated, along with the stormwater runoff. Consequently this often becomes a major source of watercourse pollution.

2.2.2 Separate Sewer System

The sewers consist of a separate system of pipes to handle sanitary sewage and stormwater runoff independently. The sanitary sewage is collected and routed to a sewage treatment plant where it is treated and the effluent discharged into the nearest convenient watercourse.

Runoff from roofs, roads and other impervious areas is collected and conveyed in stormwater sewers which discharge their load to the nearest watercourse without treatment.

The design of stormwater sewers is based on the type of area to be drained, the catchment size and its gradients, the relative impermeability, probable future developments and the rainfall patterns characteristic of that particular district. Various design methods for surface water sewers have been developed, the earliest of which were based on experience alone. These were later replaced by empirical formulae derived from measurements. Modern practice is to apply the 'Rational' (Lloyd-Davies) formula to small catchments (Bartlett (1970)), and employ the more theoretically based Transport and Road Research Laboratory Hydrograph method (TRRL (1963)) along with the new Wallingford Procedure (1981), for larger catchments.

2.3 Comparison of Separate and Combined Sewer Discharges

The nature and quantity of discharges from combined and separate sewer systems have been investigated by a number of researchers.

Burm et al (1968) compared the flow characteristics and chemical composition of combined and separate sewer discharges from an urban catchment in Ann Arbor, Michigan, USA. The concentrations of suspended solids, volatile suspended solids, settleable solids, volatile settleable solids and nitrates were all found in greater quantities in the separate storm sewer than in the combined sewer system. A further phenomena was the occurrence of a first flush effect in the separate sewer (see Section 3.3) which was not evident in the combined sewer discharges.

Tucker (1975) looked at the results from Wilkinson's study (1956) in Oxhey, England, for a separate sewer system, and Gameson and Davidson's results (1963), for a combined sewer system in Northampton, England. One aim was to determine what would happen if the areas concerned were served by each of the systems in turn. The results indicated that combined sewer overflows would generate similar solids loads and considerably higher organic loads than a separate sewer system, when set at six to nine times the dry weather flow.

Defilippi and Shih (1971) conducted a six month study in Washington DC, USA, to compare loads during storms in combined and separate sewers. It was observed that the average organic and nutrient concentrations in the separate storm sewer runoff were approximately one third of those found in the combined sewer discharges, and faecal coliform occurrence was approximately one eighth of that in combined sewer discharges.

Lindholm and Balmer (1978) studied seven catchments in Norway, of which three had combined sewers while four were separately sewered. The annual mass transport of pollutants varied considerably from one catchment to another. However, there seemed to be a correlation between pollution load and the percentage of impervious surfaces in the catchment. The increased pollutant mass transport caused by rain in catchments served by combined sewers was approximately twice the mass transport in catchments served by separate sewers.

It would therefore appear that usually, there are higher organic and nutrient loads and lower suspended solids loads in combined sewer discharges, when compared with those from separate stormwater sewers.

2.4 Current Practice and Debate

The modern approach to sewerage is to install a separate, rather than combined, sewer system. The separate sewer system has the advantage of providing firstly, a protective mechanism from sewage pollution for watercourses and, secondly, the exclusion of stormwater from a sewage treatment works. The latter can produce considerable savings in the construction and operating costs of a treatment plant. Although the separate sewer system removes the potentially detrimental effects of foul water, it does not prevent damage to the receiving watercourse from any polluting matter in the surface runoff, including accidental spillages, as these are often washed directly into the watercourse.

In the past, efforts to improve water quality management have called attention to the possibility of reducing water pollution resulting from combined sewer overflows. The most publicised remedial measure has been the replacement of combined sewer systems with separate storm and sanitary sewers, at vast expense. This proposal was based on the assumption that stormwater discharges from separate sewer systems were relatively unpolluted. Originally this was one of the main justifications for separate sewer installations. However, it has been demonstrated that stormwater alone contains a significant pollution load which may require treatment.

For the above reasons there has been, and will continue to be, much debate concerning the adoption of separate as opposed to combined, sewers.

The Technical Committee on Storm Overflows and the Disposal of Storm Sewage (1970), favoured the adoption of the separate sewer systems for new developments, but acknowledged that high pollutant flows could occur when predominantly industralised areas were drained. However, Defillippi and Shih (1971) and Nicholl and McGillivray (1978), recommended a return to combined sewer construction. The latter reached their conclusion following a study in Scotland, where highly contaminated, untreated runoff was observed discharging into streams, and where illegal connections were being made between surface and foul water sewers. Envirogenics (1971), and Medina et al (1977), both reported on the poor quality of stormwater in separately sewered catchments, and concluded that the construction of separate sewers were unwarranted because of this.

The intention of this Chapter was to give an introduction to sewer systems. The following Chapter, Chapter 3, is concerned with urban stormwater runoff quality.

CHAPTER 3

URBAN STORMWATER RUNOFF QUALITY

3.1 The Urban Stormwater Problem

Prior to the Industrial Revolution, stormwater runoff was not a significant problem, but with industrialization and urbanization, and with the concentration of populations within small areas together with the consequent increase in impermeable areas, stormwater runoff created a pollution problem.

The hydrologic effects of urbanization and its impacts on water quality have been studied by Kazi and Jalal (1977). It was concluded that urbanization causes the following:

(i) an increase in runoff (quantity and peakflow),

(ii) an increase in pollutant load in the overland flow, due to dust and dirt accumalation on urban surfaces resulting from increased human activity,

and (iii) a change in the hydrological amenities of the receiving watercourse.

Ellis (1982) subdivided the effects of urbanization into two. Firstly, the quality effects which included, an increase in pollutant concentration, an increase in mass loads, an increase in routing time and an accumulation of priority pollutants. Secondly, the quantity effects, including increased runoff volume, increase in peak runoff rate and an increase in the frequency of significant floods.

It has therefore, been well demonstrated that the pollution effect of stormwater runoff has been exacerbated by urbanization.

3.2 Development of Stormwater Quality Research

It has long been realised that urban stormwater runoff is highly contaminated. As early as 1893 Wardle observed that first storm washings contained quantities of putrescible organic matter. The first washings were found to be very foul and often contained as much organic matter as the sewage itself. Despite this realization, prior to the 1950's the quality of stormwater runoff received little attention.

During the 1950's the first serious research on the quality of surface water runoff was undertaken by Palmer (1950) in Detroit USA, Akerlinch (1956) in Sweden, Shigorin (1950) in Russia and Wilkinson (1956) in England. With the exception of Wilkinson, the work of these early investigators were restricted to the determination of quality parameters. The findings were therefore of limited use since no flow measurements were made.

Wilkinson (1956) was the first to measure stormwater flows at the same time as determining quality, for a separately sewered housing estate at Oxhey, England, and found that the quality of the stormwater runoff from this catchment area was much poorer than that of the original rainfall. Also observed was a 'first flushing' effect of contaminants in the initial phase of the hydrograph development (see Section 3.3).

The results of several years work was reported by Pravoshinsky and Gatillo at Minsk, USSR in 1969. Data were presented that showed that the BOD load discharged in the stormwater was proportional to the catchment area and to the length of the preceeding dry period.

Later, Soderlund and Lehtinen (1972) studied stormwater runoff from two urban areas in Stockholm, Sweden. A linear relationship was found between the suspended solids concentration and flow.

One of the first stormwater quality studies involving heavy metal analyses was that reported by Bryan (1972) for an urban area in Durham, North Carolina, USA. Bryan estimated a lead yield of 0.00536 kg/ha/year, with an annual yield of 0.333 kg/ha/year, and found that the major fraction of pollutants within the urban stormwater were associated with the suspended solids.

The compilation of data by Lager and Smith (1974) revealed that the annual mass of pollutants in runoff in Norway varied considerably from one catchment to another, and the data for any one pollutant varied considerably. However, no correlation could be found between the pollution load and the percentage of impervious areas.

Much of the worlds literature regarding the composition of urban runoff up to 1975 was reviewed by Loehr (1975). The paper also supported the findings of Lager and Smith (1974) regarding the wide variation in the concentration of pollutants within the runoff.

The highly polluting nature of storm sewage was illustrated by Hedley and King (1975) in the Haunch Valley, Birmingham, England. High intensity storms were found to transport the load faster than low intensity storms.

The main parameters influencing loads discharged from urban catchments were found by Tucker (1975) to be:

a) impervious area of catchment,

b) rainfall intensities and volumes,

and c) duration of the preceeding dry spell.

Tucker pointed out the above influencing factors whilst studying the suspended solids pollution loads in runoff from two suburban areas in Nottingham, England, and also observed a first flushing effect for solids.

Sediments and water quality of urban stormwater runoff were studied by Ellis (1976) for the Silk Stream catchment, North London, England. It was concluded that the fine grained sediment sludges derived from stormwater runoff could sorb ions from solution or alternatively release ions into solution. This determined the relative concentration of contaminants in solution and in suspension.

The quality of stormwater runoff from a purely residential catchment in Stevenage, Herts., England, was found to carry a significant pollutant load, particularly for ammonical nitrogen, chloride and heavy metals as a result of an investigation by Mance and Harman (1978).

Mance (1981) produced a report which reviewed the information on the quality of urban storm discharges to date. The report assessed the factors affecting the quality of stormwater discharges and also summarized the quantitative information available for the pollutant loads emanating from urban sewer systems.

The preliminary findings of the 'Priority Pollutant Monitoring Project of the Nationwide Urban Runoff Program', conducted by the United States Environmental Protection Agency, were reported by Cole et al (1984). Nineteen cities throughout the United States participated. The most likely sources of 24 of the selected pollutants were given in the report, including heavy metals, the potential risk to human health together with the potential risk to aquatic life.

Recently more detailed studies have been undertaken into specific aspects of the stormwater runoff problem. These studies will be discussed later in the appropriate Sections.

Polluted stormwater discharges are difficult to assess due to their unpredictability and the wide qualitative variations which occur. Table 3.1 is a compilation of data to show the variations for stormwater quality found in the UK (from Ellis (1982)).

Source: Ellis (1977), Fletcher et al (1978), Gavens et al (1981) Hedley and Lockley (1975), Mance and Harman (1978), National Water Council (1978), Pope et al (1978), Tucker and Mortimer (1978), Wilkinson (1956).

Table 3.1 Reported variations for stormwater quality discharges in the UK. (Ellis (1982))

3.3 First Flush Effect

Previous quality studies, including those by Tucker (1975), Wilkinson (1956), Weibel et al (1964 and 1969), Ellis (1976), Adams (1978), Mance and Harman (1978), Droste and Hart (1975), Pope et al (1978 a and b), Wilber and Hunter (1975) and Colwill et al (1984), have observed an initial peak flushing of contaminant levels which occur prior to the maximum flow of the runoff hydrograph from urban areas. The primary peak has been termed the 'First Flush Effect', see Figure 3.1, and has been attributed to the remains of contaminants deposited in the below ground system from previous runoff events (Ellis (1979) and Mance and Harman (1978)).

The term 'first flush', now in general usage, has been defined by Mance (1981) as follows:

> 'Following the onset of rain there is an initial flow of stormwater (storm sewage in a combined sewer system) along sewers and urban watercourses that is of significantly poorer quality than any subsequent flow, and this is referred to as the first flush'.

Essentially it is a peak concentration of pollutants before the maximum discharge occurs.

The first flush phenomena was first observed by Wilkinson (1956) in the Oxhey catchment where between 43% and 50% of the polluting matter was discharged by 29% of the water within the first 30 minutes of the flow.

Figure 3.1 The first flush phenomenon (Tucker (1975)).

Mance and Harman (1978) confirmed these general observations made by Wilkinson (1956), where most of the storms analysed within the Shephall catchment displayed a first flush of water which was more polluting than the rest of the storm. However, in many of the storms the runoff water remained fairly dirty for a considerable time after the first flush and water discharged throughout storms remained more contaminated than the first flush of other storms. It was therefore apparent that the catchment area was not rapidly washed clean by the first flow of water.

Ellis (1976) made the same observations for the Hendon catchment as Mance and Harman (1978) did for Shephall, and commented that the suspended solids concentrations generally fell after approximately 36 minutes of flow, which was the time of concentration of the catchment. Mance (1981) also concluded that the first flush had a duration which approximated to the time of concentration of the particular sewer system, and also stated that the mass flow of pollutants may be significant even after this period of discharge. Hedley and King (1971) considered the first flush in terms of the proportion of the storm load discharged (total load minus estimated dry weather load), and it was observed that between 40% and 80% of the storm load was discharged within the time of concentration.

Later studies at the Oxhey catchment (Ellis (1974) and Harrop (1984)) have also observed a first flush of contaminants. This initial peak of pollutants was not, however, a dominant feature and was more marked after a lengthy antecedent dry period.

3.3.1 Quantification of the First Flush

Colston (1974) described the first flush effect as an initially high pollutant concentration followed by decreasing concentration as the storm proceeded. However, concentration is dependent on flow, and therefore Griffin (1977) developed a quantitative measure for defining the first flush. Cumulative percentages of the total storm load and flow were plotted against the percentage of time elapsed, the first flush occured when the incremental load exceeds the incremental flow during any time interval:

i.e. $$\frac{\text{Incremental Load}}{\text{Incremental Flow}} > 1.0$$

The above ratio is a quantitative measure of the magnitude of the first flush.

An alternative technique for identifying the first flush has been suggested by Tucker (1975). This requires a plot of the cumulative mass discharge (instantaneous concentration multiplied by flow) and the cumulative square of the flow for each individual event. Tucker (1975) states that typically this yields a straight line for most of the storm, but has an initial period of rapid mass discharge. The mass of the first flush is obtained by extrapolating the straight line to the y-axis, where the intercept lies, the mass of the first flush is given. The mass of the first flushes for the Chelmsley Wood study were calculated in this way and are presented in Section 12.7.

3.3.2 Discussion on the First Flush

Although the phenomenon and validity of the first flush is now being increasingly questioned (Ellis (1982)), there is some evidence to suggest that when it does occur, the first flush approximates to the time of concentration of the sewer system (Ellis (1979)).

The initial first flush of runoff and pollutant loadings would appear to be a result of in-pipe sources i.e. purging of deposited loads from previous storms, as well as from early roof runoff within the system. In storm sewers there may be a tendency for solids to settle out during the latter stages of a storm as the flow tapers off. These solids which settle out undoubtedly contribute to the first flush effect (Wilber and Hunter (1975)). Adams (1978) also stated that the prime peak was due to the solids settled out and lodged within the system from antecedent storm events, these were rapidly and efficiently flushed out on the rising limb of the storm wave. However, those sections of the sewer pipes which could be visually examined in Chelmsley Wood showed little evidence of in-pipe deposition and therefore the more likely prime source of the first flush is probably roof runoff (Harrop (1984)).

During a storm event the first runoff into the sewer system will be that coming from the roofs, which gives a very quick response time but contains few pollutants. This is followed by the contributions from the roads etc. which are of a slower response time but are high in pollutants, thereby producing a peak of pollutants after the start of the storm (Butler (1981)). However, it has recently been stated that the roof runoff contains many pollutants and that this roof runoff, together with gully pot discharges accounts for approximately 60% of the first flush (Ellis (1984)).

Fletcher et al (1978) also found that the roadside gully pots were a major contributing factor to the first flush events, due to the anaerobic digestion of the gully pot liquor.

As particular material mobilization is dependent on flow velocities, the first flush phenomenon is not a common feature of all storms but is related to the character of the rainfall/runoff event. Thus, although high suspended solids levels are normally encountered during the initial stages of the event, peak levels generally coincide with either peak flowrate or peak rainfall intensity (Colwill et al (1984)).

In conclusion, a first flush effect has been observed in a number of investigations. It is a variable phenomenon that does not always occur. Even when it does occur, subsequent flows are often of poorer quality. For separate sewer systems it is reasonable to equate the duration of the first flush with the time of concentration of the catchment (Mance (1981)).

3.4 Secondary and Multiple Peaks

Some workers, including Ellis (1976), Adams (1978) and Harrop (1984), have noted double and multiple peaking of contaminants during stormwater runoff events. The prime peak (as discussed in Section 3.3) occurs early in the hydrograph with, or even before, the peak discharge. The contaminant levels now fall and then rise to a second peak on the recessional limb of the hydrograph (Adams (1978)). The second subsidiary peak represents fresh sediment introduced into the below ground system from the erosion and entrainment of material lying on roofs, roads, paths and driveways and which is often delayed behind the prime peak (Ellis et al (1981) and Adams (1978)).

The gully pot storage component has also been suggested to be the principal factor in explaining the occurrences of the secondary pollutant peaks observed at the outfall pipe (Harrop (1984)).

Harrop (1984) observed secondary and multiple peaks for most contaminants during storm runoff events. The secondary peaks tended to be considerably diminished. Such peaks were explained by delayed above ground impervious surface runoff contributions entering the system (Ellis (1976)). Alternatively, settling and deposition can take place within the pipe system and contribute to a reduced secondary peak as well as to the first flushings of subsequent runoff events. In more than 90% of the observations the secondary peaks were independent of any subsequent flow patterns in the relevent storm.

As in the case of secondary peaks, the multi-peaks occured independently, in most instances, of any rainfall/runoff processes, during the particular storm after the initial peak discharge. The delayed peaks may be a consequence of previous runoff from both gardens and playing fields via french drains, hence giving a slower time of concentration.

The multi-peaks would therefore appear to be derived from previous surface runoff or possibly throughflow, which would explain the lag times observed for their delivery. The infrequent and abnormal peaking of loadings within the system can only be explained as a result of sporadic anthropogenic inputs (Harrop (1984)).

3.5 Effect of Stormwater Runoff on Receiving Watercourses

The effects of polluted stormwater discharges are difficult to assess due to their unpredictability and the wide qualitative and quantitative variations which occur.

Urban stormwater runoff can create and contribute to a variety of problems, including, direct pollution of the receiving water, overloading of treatment facilities, and the impairment of sewer and catchbasin (gully pot) functions.

Table 3.2 (taken from Harrop (1983)) illustrates the established water quality control criteria for drinking water and fresh water fishing. When compared with Table 3.1 for stormwater runoff pollution levels, it is clear that stormwater runoff is likely to be detrimental to the quality of the receiving water. Stormwater can contribute concentrations in excess of one hundred times the levels that are detrimental to the health of freshwater fish and four hundred times greater than the standards required for the abstraction of drinking water.

The mass loadings of solids can reduce light penetration, cause the smothering of substrates and act as host carriers for a variety of sediment associated contaminants. The highly toxic heavy metal discharges, particularly lead, chromium, zinc and copper, are substantially above that specified by most national standards. Total concentrations of zinc and copper are almost three times that of the tolerable levels specified by the European Inland Fisheries Advisory Council (EIFAC) for freshwater fish.

Table 3.2 (a) EEC standards required for surface water intended for the abstraction of drinking water. (Harrop (1983)).

Table 3.2 (b) EIFAC tentative standards for freshwater fish. (Harrop (1983)).

Extensive studies by the AVCO (1970) and the APWA (1969) have provided much valuable information on the overall problem of water pollution resulting from urban runoff. Both studies stressed the importance of the 'shock loading' that the stormwater can put into the receiving streams.

Wanielista (1977) concluded that the polluting effects of urban runoff on recieving water quality were variable and site specific. They would depend upon the site characteristics and on the receiving water conditions.

3.6 Treatment of Urban Stormwater Runoff

A number of authors have shown that the annual pollution load of stormwater can equal that exerted by treated domestic sewage effluent, (Weibel et al (1964), Bryan (1972), Whipple et al (1974) and Field and Lager (1975)). Significant advances in pollution abatement cannot, therefore, be achieved by improving the treatment of domestic sewage and industrial wastes alone. Techniques for improving the quality of urban stormwater runoff must be employed in order to achieve more than minimal reduction in the pollution of surface waters. However, the major difficulty regarding treatment of urban stormwater is the intermittent nature of discharges, which tend to occur for short periods of time and have large total volumes. The provision of a plant to treat stormwater, at its unrestricted flowrate, is not as yet financially viable.

Treatment of the effluent from combined sewers is becoming relatively common (Field and Lager (1975), Lager (1974), McPherson (1974)), the procedure being similar to conventional sewage treatment, but with storage facilities forming an integral part.

Hedley and Lockley (1978) evaluated the use of retention tanks in Birmingham's sewerage system. The effects of these concrete retention tanks, constructed at the outfalls of three existing storm sewage overflows, were studied over a five year period. The retention tanks were found to operate successfully, while being financially attractive and adaptable, and could provide an immediate expedient for the control of pollution from existing combined and partially separate sewer systems.

Simple settling has been shown to be an effective means of mitigating the effects of stormwater runoff pollution. Cordery (1976) conducted experiments in the laboratory to study the effects of settlement on the quality of stormwater runoff. It was shown that for a typical urban catchment, a retention time of approximately one hour resulted in the removal, through settlement, of similar amounts of pollutants to that which would have been removed by the treatment of secondary sewage effluent from the same catchment. The cost of this treatment was calculated to be far less than that for tertiary treatment of a secondary sewage effluent.

Evans et al (1968) found that settling times of greater than one hour were needed to achieve a noticeable improvement in the quality of stormwater runoff. If retention times of less than one hour were employed, settling was not effective in reducing either BOD, COD, nitrogen, phosphates, solids or some bacteria (eg. total coliforms). Whipple and Hunter (1981) studied the efficiency of detention basins, and found that the settleability of specific pollutants varied widely, and that for the runoff from different areas there was a considerable difference in the settleability of each class of pollutant.

Wooldridge (1981) used a computer simulation to study the behaviour of urban storm drainage networks with off-line and on-line storage tanks. It was observed that the volume of storage required, for noticeable improvement in runoff quality, was dependent upon the shape of the catchment, and that the storage volume of off-line tanks was significantly less than for on-line ones.

Storm generated pollution is not solely a problem of large metropolitan communities, but also relates to small urban catchments. Oliver and Grigoropoulos (1981) looked at source control of storm generated pollution. A small urban area in Rolla, USA, was studied which included a small recreation lake that provided detention and natural treatment for the runoff studied. It was found that the lake could be used as an effective means of managing stormwater runoff, since it not only effected an immediate improvement in runoff quality but had sufficient capacity for the removal of pollutants on a long term basis. Cordery (1976) also observed that stormwater held for several days in lakes and ponds, which were a part of the natural landscape of urban Sydney, Australia, underwent considerable aeration and deposited much of its suspended load.

Heaney and Sullivan (1971) suggested another type of source control for stormwater runoff pollution. The proposal was to reduce the number of catchpits (gully pots) in a particular area, since these are a source of pollution in their own right (see Section 5.4.1).

In conclusion stormwater runoff from urban catchments requires control and treatment if substantial improvements in the quality of receiving streams is to be achieved. This may involve source or collection system control, storage of urban stormwater, treatment of runoff or an integrated system of control and treatment. However, according to Ellis (1982), structural storage facilities provide the most reliable control systems.

3.7 Modelling Urban Stormwater Runoff

Storm runoff from urban areas can adversely effect water quality in receiving streams. Unless urban stormwater runoff can be treated or controlled many receiving waters will be prevented from becoming 'fishable and swimmable' as suggested in the US Water Pollution Control Act Amendments of 1972 (Jewel and Adrian (1981)). In order to determine where and when to control stormwater runoff it is necessary to assess its impact and estimate the effects of various control measures, tasks that would be extremely difficult using measured data alone. Therefore, researchers have used simulation models to predict the quantity and quality of stormwater runoff and how it would effect the environment under controlled and uncontrolled conditions.

Considerable research, particularly in the USA, has been directed to the statistical analysis of water quality data to quantify pollution loads for more effective water resource planning. With the advent of powerful computers the deterministic modelling of stormwater runoff quality has become increasingly attractive and models such as the Storm Watershed Management Model, abbreviated to SWMM (1971) and the Storage Treatment Overflow and Runoff Model, abbreviated STORM, have been developed.

These models enable the research engineer to simulate the behaviour of pollutants in storm sewer systems and provide the planner with objective guidance in decision making.

Both SWMM and STORM assume that the runoff of a particular pollutant from a given area is directly related to the instantaneous discharge from that area and the amount of pollutant available. Although this assumption may be taken as giving a reasonable indictaion of water quality it can lead to considerable errors. Such models have been found to provide good simulations of flow volumes but poorer results for quality simulations, except where specifically calibrated for a particular catchment area (Harrop (1984)). Consequently there is value in studying runoff from a reasonably small urban area to see if the predictions can be refined.

Mathematical models concerning urban stormwater runoff have been developed for certain catchments within the UK. Tucker and Mortimer (1978) developed a model of solids generation based on the concept of contributions of total suspended solids concentrations from both the 'first flush' and the 'subsequent' solids. The model was found to produce a reasonable agreement with recorded data from two separately sewered suburban catchments in Nottingham, England.

Price and Mance (1978) produced a model to predict the runoff of suspended solids from an urban catchment. The model was applied to observed events on a catchment at Stevenage, Herts., and the results indicated that the model provided a realistic description of the runoff, with a good agreement between predicted and observed mass flows.

Pratt and Harrison (1982) developed the Trent Urban Runoff Simulation Model (TURS) from observed catchment characteristics, to predict storm discharge hydrographs for the Clifton Grove catchment in Nottingham. The model, at that time, was shown to over predict peak discharge and runoff volume. However, the model was used to illustrate the relative importance of road and roof runoff at various times during the outflow hydrograph. An earlier version of TURS (Fletcher and Pratt (1981)) was used to predict the discharge of original, stored gully pot liquors and their influence on total outflow quality.

Harrop (1984) developed a model for the Oxhey catchment, relating storm characteristics to runoff water quality through multiple regression analyses. It incorporated both the above and below ground phases of contaminant removal from the catchment surface. Results indicated that the predominant variables which interact on the road surface and determine pollutant removal rates were active throughout the system, although there was a marginal reduction in the influence of rainfall characteristics below ground. Using the multivariate analysis technique, Harrop found a strong correlation between washoff loadings, and total surface runoff and event duration. In addition, for lead and cadmium, flow and storm duration explained more than 90% of the observed variance and 79% of the variance for zinc concentrations.

In conclusion, there appear to be numerous urban stormwater pollution models currently available. However, some are very specialised and can only simulate certain pollutants, while others are site specific. The potential uses for a general model as opposed to a catchment specific one, are many fold. In addition to being operated to obtain a better understanding of the processes at work within a catchment, a generalized model could be used as a predictive tool for, amongst other things, evaluating the potential effects on receiving watercourses, the value of cleansing activities and the effectiveness of legislation on vehicle emissions.

The use of any model will depend upon the desired results, availability of input and calibration data and the knowledge of the users.

Having discussed urban stormwater runoff quality, the heavy metal contribution in particular, will now be discussed in the next Chapter, Chapter 4.

CHAPTER 4

HEAVY METALS AND URBAN STORMWATER RUNOFF

4.1 Introduction

The term 'heavy metal' is a broard one and includes metal elements of atomic weight higher than that of sodium (23) and having a specific gravity in excess of 5. It can therefore be applied to over 70 metallic elements of which only a small number are of critical environmental concern and include: antimony, copper, cadmium, mercury, tin, lead, chromium, cobalt, zinc and nickel.

The identification of those heavy metals which can be classified as toxic or hazardous is however, complicated by the fact that certain heavy metals are essential as trace elements for the normal functioning and growth of living organisms. The problem is further compounded in that the difference between the concentrations of a heavy metal required for adequate nutrition and that which is known to produce symptoms of toxicity is relatively small and for certain metals is not well defined (e.g. nickel, copper and zinc).

4.2 Sources of Heavy Metals

The principal sources of heavy metal contamination in the environment are reasonably well recognized and have widely been documented (Davies (1977), Thornton (1980) and Greenland and Hayes (1980)). The main anthropogenic sources of heavy metal emissions to the environment have been summarized by Haines (1982), and are as follows:

(i) urban industrial aerosols created by the combustion of fuels, production of base metals, iron and steel production and other industrial sources,

(ii) mining wastes,

(iii) industrial and agricultural chemicals,

(iv) disposal of liquid gases and semi-solid wastes from industrial activity,

and (v) disposal of sewage sludge.

Metal incidence in the natural environment also arises from the natural weathering of metal bearing rock formations.

The main sources of heavy metals to urban stormwater runoff according to Horkeby and Malmquist (1977) have been taken to be exhausts from vehicles, wearing of tyres and asphalt surfaces and the corrosion of vehicles and building surfaces. The sources and transport of heavy metal pollutants in urban stormwater are shown in Figure 4.1.

The principle sources of the heavy metals studied in this thesis, to the stormwater runoff system are summarized below.

Iron and ferrous derivatives have been found in de-icing salts and vehicular corrosion, which is increased by road salting. The annual peak of iron content in motorway runoff has been shown to occur some 5 - 6 weeks after the peak of salting to the road surface. This was also found to correlate with vehicular corrosion rates (Bickmore and Dutton (1984)). Another important source of iron content is that from the soil (Klein et al (1974)).

The major source of lead in the environment comes from the combustion of alkyl lead in motor fuels (see Section 5.3.2.4.2.2). This potential lead pollution is to be reduced in 1986 when the lead component of petrol will be reduced from 0.4 to 0.15 gms/l in the UK. Lead is also found in de-icing salts and as additives and pigments in painting and staining products (Cole et al (1984)).

Figure 4.1 Sources and transport of heavy metals pollutants to urban stormwater. (Malmquist (1975))

Zinc is employed in the manufacture of tyres, in the form of ZnO as an accelerator in vulcanization. The average zinc concentration in tyres has been found to be 0.73%, and the depostion rate was estimated at 0.003 gms zinc/veh km in the USA by Christensen and Guinn (1979). In Sweden where zinc and copper are used in roof fittings, it was found that a considerable amount of zinc and copper found in stormwater originated from the corrosion of these building materials (Malmquist (1975)).

Zinc and cadmium have also been found together in lubricating oils as part of additives such as zinc dithiophosphates, where the cadmium can be an impurity in the original zinc used to prepare the additive (Lagerwerff and Specht (1970)). Zinc and cadmium are naturally associated with one another in soils (Haines (1982)) and zinc is also found in de-icing salts.

Vehicles are again the most probable major source of copper to urban stormwater. Copper is a common constituent of piping and other components of engines and chasses (e.g. thrust bearings, bearing plates and brake linings). Mechanical wear and tear deposits these materials as fine dust to the roadway and therefore to stormwater runoff (Harrison (1978) and Ward et al (1977)). Copper is also found in de-icing salts and is commonly used in algicides (Cole et al (1984)). Other sources include the combustion of coal and the use of phosphate fertilizers.

The major source of chromium is again from vehicles and de-icing salts. Hedley and Lockley (1975) found that the de-icing salt was a major source of chromium and nickel to urban stormwater runoff. It is also probable that some chromium is derived from the soil (Harrison (1979)). Chromium is a component of motor vehicles (e.g. rocker arms, crankshafts and rings and plating of motor vehicle parts) (Cole et al (1984) and Shaheen (1975)). The attrition of these surfaces together with engine wear, result in fine particles being deposited on the road surface and are later picked up by urban stormwater runoff.

Turner (1971) postulated that the yellow painted (lead chromate) restriction lines on roads may be a source of both lead and chromium. However, later in 1979, Harrison disproved this theory by finding similar amounts of chromium in street dusts from rural areas where there were no such parking restriction lines. It would therefore appear that lead chromate paint makes very little contribution to the lead and chromium content of street dust unless it becomes abraded/eroded enabling paint particles to be released.

Nickel and chromium have been found to be present in brake linings and are released to the roadway surface materials by abrasion (Harrison (1979)). Nickel and chromium are also frequently used in chrome plating. Nickel is also a product from fossil fuel combustion (Cole et al (1984)) and from the corrosion of stainless steels (Burrell (1974)).

Cadmium is often released into the environment in association with lead and zinc, and is present in soils, vegetation and mans food in small amounts. The presence of cadmium in the environment stems mainly from mans activities and the metal industries contribute a major source of cadmium in the environment. Cadmium is also widely used in modern industrial processing, in paint, batteries, plastics, pigments, thermoplastic stabilizers, fluorecent and television tubes (Herm (1972)).

Lagerwerff and Specht (1970) analysed three samples of lubrication oils and found that the cadmium levels ranged between 0.2 and 0.26 ppm and in three diesel oils ranged from 0.07 to 0.10 ppm. Also reported was a value of 20 - 90 µg/g cadmium in car tyres as a probable result of zinc-diethyl carbonate, where cadmium is a contamination product in the process of vulcanization.

It has been widely found that motor vehicles and de-icing salts are a major source of heavy metal pollution to urban stormwater runoff, (Lagerwerff and Specht (1970), Harrison (1979), Christensen and Guinn (1979), Cole et al (1984) and Ward et al (1977)).

Other major sources include the combustion of fossil fuels, metal plating industries (Harrison (1979)) and impurities in certain agricultural chemicals (Lagerwerff and Specht (1970)).

4.3 Toxicity and Environmental Consequences

The effects of heavy metal pollution in the environment have received considerable attention over the past decade. Initially, studies on health effects concentrated on heavy metals in the air or drinking water, but it is now generally recognized that settled dust in urban areas can represent an important source of toxic metals, particularly to young children. Additionally, as rainfall washes the road surface the dust acts as a major contributor to heavy metal pollution in urban stormwater and eventually to receiving waters. The transport pathways and effects of these heavy metals depend on a range of physical and chemical properties, including pollutant concentration, the size spectrum of the heavy metal containing particles and the chemical form in which the metals occur (Hamilton (1984)).

Environmentalists are concerned that chronic exposure to doses of heavy metals, which are insignificant in themselves, may nethertheless be harmful. Priority should be given to minimizing the general public exposure to these metals and it is regretable that there is no statutory control in this area. Even where legislation exists the levels which are allowed are often much to high (Waldron (1975)).

All heavy metals are potentially harmful to most organisms at some level of exposure and absorption. The susceptability of a particular organism to the toxic effects will depend on many factors including age, surface area, population structure of the organisms and the metal ion concentration together with the chemical environment. The relative toxicities of the various heavy metals vary, and soluble forms are normally highly toxic and more dangerous than the solid associated forms. Thus in stormwater runoff the dissolved phase is the potentially more toxic, whilst suspended solids may only represent a transport phase and subsequently becomes a chronic exposure source for organisms only after deposition and accumulation in the receiving water (Morrison (1983)).

Heavy metals are also toxic to man. The toxicity varies significantly depending on a wide range of factors, which include the route of entry into the body, nutritional factors, age and sex. For some of the more toxic heavy metals, the chemical form of the metal intake is also important. Table 4.1, adapted from Horkeby and Malmquist (1977), summarizes the effects on flora, fauna and man, of the heavy metals studied. The Table only relates to the pure metals, whose toxic effects can be different from those of the metal compounds. The maximum permitted concentration in drinking water and measured concentration in sludge wastewater, drinking water and ambient air are given in Tables 4.2 and 4.3.

Large fluxes of heavy metals from stormwater discharges may therefore be hazardous to both the fauna and flora of a receiving stream. The studies of Galcher and Urech (1983) have shown that 10 μg/l copper and 50 μg/l zinc can cause dramatic reductions in phytoplankton and zooplankton in environmental systems. Since many urban stormwater discharges greatly exceed those dissolved heavy metal concentrations, the toxicity may well be above the 'safety limits' and certainly above acceptable emission standards (Morrison (1983)).

Table 4.1 The effects of specific heavy metals on Flora, Fauna and Man.
(adapted from Horkeby and Malmquist (1977))

Table 4.2 Maximum allowed concentrations of metals in drinking water according to the standards of USSR, WHO (Europe) and Sweden in µg/l. (Horkeby and Malmquist (1977))

Table 4.3 Metal concentrations in sludge, wastewater and drinking water from Swedish sewage and treatment plants. (Horkeby and Malmquist (1977))

Laveskog et al (1976) (a)
Aronsson (1977) (b)
Aronsson (1974) (c)

4.4 Heavy Metals in Urban Stormwater Runoff

In recent years there has been growing concern about the quality of runoff from rainfall and snowmelt in urban areas. A major part of this concern has centered on trace elements (e.g. Bryan (1974), Newton et al (1974), Horkeby and Malmquist (1977) and Wilber and Hunter (1977)). Many trace elements are known to be toxic at certain concentrations to a wide range of aquatic plants and animals (McKee and Wolf (1963)).

Urban stormwater is known to have a high content of heavy metals (Mance and Harman (1978), Ellis et al (1981), Colston (1974) and Newton et al (1974)). Table 4.4 summarizes the results of several investigations. Although extreme variability is shown, it is certainly obvious that the amounts of heavy metals in urban stormwater runoff are quite significant. Concentration of metals range from relatively low values to those equalling or surpassing concentrations found to be toxic to certain species of freshwater organisms (Schroeder (1965)).

The impact of polluted waters from non-point sources, including urban surface runoff on receiving waters is considered by many researchers to be of a serious cause for concern. Large fluxes of heavy metals from stormwater discharges may be hazardous to both fauna and flora of a receiving stream (Galcher and Urech (1983)).

METAL	MIN.	MAX.	MEAN	REFS.*
IRON	1.0	85		1
			1.0	3
	1.3	58.7	12	4
		47	4.2	5
	2.4	24	8.2	6
	20	62	38	6
LEAD	0.25 26			2,7,8,9,10
	0.05	3.09	0.45	11
	0.10	2.86	0.46	4
	0.10	1.85	0.67	12
	0.10	1.20	0.36	6
	0.42	1.29	0.09	13
			0.46	14
			0.09	15
			0.23	16
			0.21	17
			0.41	18
			0.40	19
			0.14	26
			0.20	3
			0.37	20
		3.70	0.20	17
		2.20	0.21	5
ZINC	0.008	4.60		4,9,10,22
	0.177	1.09	0.62	13
	0.09	4.60	0.36	4
	0.06	0.65	0.18	6
	0.15	1.10	0.40	6
	0.06	0.88		24
			0.36	14
			1.60	25
			0.27	17
			0.57	18,19
			0.16	26
			0.46	3
			0.28	20
		1.63	0.27	17
COPPER	0.007	1.41		4,10,13,22
	0.001	4.62	0.15	13
	0.04	0.50	0.15	4
	0.01	0.09	0.03	6
	0.02	0.12	0.54	6
			0.15	14
			0.46	25
			0.03	17
			0.19	18

Table continued overleaf

METAL	MIN.	MAX.	MEAN	REFS.*
COPPER			0.31	19
			0.27	3
		0.35	0.028	17
CHROMIUM	0.06	0.47	0.23	4
			0.07	6
			0.34	6
	0.015	0.044	0.03	13
			0.23	14
			0.16	25
			0.0025	10
NICKEL	0.09	0.29	0.15	4
	0.025	0.15	0.08	13
			0.15	14,25
			0.24	3
			0.05	6
CADMIUM	0.0008	0.008		27
			0.006	3
			0.016	6
			0.01	6

Table 4.4 Concentrations of total heavy metals in stormwater runoff. (mg/l)

*

1 Ellis and Alley (1979)
2 Hedley and Lockley (1975)
3 Horkeby and Malmquist (1975)
4 Colston and Tafuri (1975)
5 Collins and Ridgeway (1980)
6 Alley and Ellis (1979)
7 Sylvester and De Walle (1972)
8 Pitt and Amy (1973)
9 Shaheen (1975)
10 Mance and Harman (1978)
11 Reinertsen (1981)
12 Bryan (1972)
13 Wilber and Hunter (1975)
14 Colston (1974)
15 Hem and Durum (1973)
16 Newton et al (1974)
17 Mance (1981)
18 Lindholm and Balmer (1978)
19 Malmquist and Svensson (1977)
20 Christensen and Guinn (1979)
21 Morrison et al (1984)
22 Whipple and Hunter (1979)
23 Pope et al (1978)
24 Ellis (1982)
25 Klein et al (1974)
26 Roberts et al (1979)
27 Dauber et al (1978)

Heavy metal concentrations do vary considerably with place and time, and a mean concentration for one area will tell almost nothing about the concentration from another area. The difficulty when using much of this information (e.g. Table 4.4) in any quantitative way, is that concentration of heavy metals in urban runoff are dependent upon a number of factors, some of which are (Wilber and Hunter (1975)):

(i) the intensity and duration of the storm,
(ii) the length of the antecedent dry period,
(iii) the general effectiveness of waste removal in the streets,
(iv) composition of the storm sewer,
and (v) land use.

As a result, sparadic or fragmentary data may give results widely different from those generally characteristic of the basin.

Urban surface runoff may include pollutant or natural material that is available for transport within the catchment area. Increased urban surface impermeability results in both increased runoff and heavy metal loadings.

4.5 Motorway/Road Surface Runoff

Information on motorway runoff quality is relatively scarce and there is little detailed information. Hedley and Lockley (1975) studied the A38M Aston Expressway in Birmingham, which had a traffic density of 57,500 vehicles/day. The ranges of average concentrations of specific heavy metals, taken from a 12 month sampling period, are given in Table 4.5.

Pope et al (1978 b) studied three small subcatchments on the M1, 3 km south of the Toddington service area, and Mance (1982) studied a catchment at Basils Road, Stevenage, that carried 1000 vehicles/day. The data from these studies are summarized in Table 4.6 and Table 4.7 is a compilation of data for motorway/road surface runoff from a number of authors. The predominant effect of motor vehicles is clearly demonstrated when the loadings per million vehicle km per year is considered. Unfortunately very few studies of stormwater quality provide data on traffic densities (Mance (1982)).

Bickmore and Dutton (1984) have shown that on average 75% by weight of contaminants available to enter motorway runoff were derived either directly from vehicles or indirectly through road surface degradation. The remaining 25% consisted largely of de-icing salt material. It was also concluded that motorway runoff does not generally have an adverse effect on the receiving body of water, due to the diluting effects of the receiving water.

Table 4.6 Summary of water quality data reported for highway drainage. (Mance (1982)).

METAL	MIN.	MAX.	MEAN	REFS*
IRON	8.5	182.9	75	1
		1.68	0.64	2
	0.67	440		3
LEAD		2.9	0.34	4
		3.09	0.45	5
		2.10	0.15	6
		4.94	10	1
			0.3	7
	0.316	2.874	0.63	8
	0.10	8.015	0.55	8
ZINC	0.22	3.1		6
			0.25	4
	0.65	8.01	3.55	1
			0.29	7
	0.275	4.047	1.13	8
	0.116	3.425	1.176	8
	1.2	1.9		9
COPPER			0.05	4
	0.12	1.7		6
	0.10	1.44		1
			0.08	7
	0.003	0.38		3,4
	0.007	0.03		8,9
CHROMIUM	0.018	0.85		9
			0.38	1
		0.018	0.085	8
NICKEL			1.55	1
CADMIUM			0.0034	4
	0.0005	13.73		3,4,9
	0.0003	0.102	0.0152	8
	0.0003	0.039	0.0114	8

Table 4.7 Concentrations of total heavy metals in road surface/motorway runoff (mg/l).

*

1 Hedley and Lockley (1975)
2 Extence (1978)
3 Bourcier and Sharma (1980)
4 Dauber et al (1978)
5 Reinertsen (1981)
6 Mance (1982)
7 Pope et al (1978 (a))
8 Colwill et al (1984)
9 Pope (1980)

4.6 Particulate and Soluble Metal Concentrations

Many of the heavy metal studies which have been carried out do not differentiate between particulate and dissolved metals. When relating metal levels to toxic effects it is important to recognize that there are often considerable loading of dissolved metals in storm discharges. In addition metals may be mobilized from the particulate phase to the dissolved phase, cadmium in particular has been shown to be readily solubilized from road sediments (Revitt and Ellis (1980)). Thus a knowledge of heavy metal kinetics and speciation (i.e. the association in which the contaminants exist on the road surface prior to removal by runoff) is important if advances are to be made in evaluating the relative toxicity of urban non-point discharges (Morrison (1983)). The particulate/soluble differentiation provides the most basic expression of this influence and was used in this study.

Alley and Ellis (1978) analysed rainfall runoff for both the dissolved and total heavy metal phases. The average concentration for the two sites are given in Table 4.8. From consideration of the Table it can be seen that the particulate phase was more prevalent than the dissolved phase, with the ratio of particulate to dissolved phase ranging from 1.5 to 125 and averaged 20.

Morrison et al (1984) looked at the heavy metal concentration within two storms, and the variations of heavy metals between the dissolved and suspended solid phases throughout the duration of two storm events. The heavy metal concentrations are illustrated in Table 4.9, whilst the flow weighted loadings are given in Table 4.10.

From consideration of Table 4.10 it can be seen that greater loadings of zinc and cadmium occurred in the dissolved rather than the particulate phase, whereas copper was distributed between both phases and lead was predominantly particulate associated. The preference for the dissolved phase was therefore Zn > Cd > Cu > Pb. For all metals the dissolved phase increased in proportion throughout both of the storms and for lead, the dissolved phase became quite significant towards the end of the second storm. Zinc, lead and copper displayed similar average concentrations within the suspended solid phase, suggesting a continuous source or input (Morrison et al (1984)).

4.7 Variations in Heavy Metal Loadings during Storm Events

It is not fully understood how urban heavy metal source loadings are reflected in the stormwater discharges at the outfall of the catchment pipe system. A first flush of highly turbid water, with a duration of some 20 to 30 minutes, has been observed at the beginning of storm events (see Section 3.3). Ellis (1982) has discussed the importance of the time of concentration for the catchment, which is considered to explain the lack of the first flush noted in some events. From these observations heavy metals might be expected to be concentrated in the first part of the storm event (Mance (1981)). This assumption is also based on the concept of the strong affinity of metals for stormwater suspended solids (Bourcier and Sharma (1980) and Wilber and Hunter (1979)), which often parallels the storm hydrograph. However, this assumption has largely been refuted by direct measurements throughout individual storms (Revitt et al (1981)). This apparent discrepency in views would suggest that metal inputs are being delivered from a variety of sources and are being mobilized at different rates and at different times during the storm event and are thus loaded on the hydrograph at different times.

Of the storms analysed by Revitt et al (1981), some 20 to 30% of the total metals were discharged within the first 20 minute period for two storms. In the third storm, however, there was a pronounced first flush in the case of cadmium with 43% of the metal discharged during the same time period, in comparison with only 4 to 7% in the case of the remaining metals. The results would suggest that there had been no accumulation of metal rich liquors in gully pots prior to the storm events and that the metal levels were maintained by a continuous process of sediment flushing throughout the storm. Variations of metal concentrations (μg/g) with time showed distinctive patterns for each storm event although for each individual storm there were identical temporal distributions for copper, iron, lead and zinc, despite occasional exaggerated peaks. The complexity in metal peak and trough patterns could be related to spasmodic release from the sewer system of fungal mats and their associated particles (Ellis (1979)).

Cadmium concentrations displayed distinctive temporal patterns with pronounced first or delayed flush. This unique behaviour could be related to a source related effect or due to processes occcurring within the system, also the ready removal of cadmium into the soluble phase may partly explain its non-coincidence (Revitt and Ellis (1980)).

Heavy metals for the Shephall catchment (Mance and Harman (1978)), were found to be predominantly in the particulate phase and as a consequence followed a similar pattern, if less consistent, to the suspended solids concentrations and mass flows. In contrast, the soluble determinands displayed an initial increase in concentration that was followed by a rapid and sustained decrease, although the mass flow still responded to increases in flow.

Table 4.11 summarizes the quality of runoff from the Shephall catchment. Linear relationships were found between suspended solids concentrations and those of chloride and heavy metals within each individual storm event. However, these relationships varied unpredictably between storms, and in contrast, data from an apparently similar catchment of Chelmsley Wood produced a general linear relationship which was consistent for all storms studied (Mance (1981)). The maximum concentrations of associated heavy metals for the Shephall catchment were found to be associated with the prolonged dry weather in the summer months.

Alley and Ellis (1978) studied trace elements in runoff from several urban communities in Denver, USA. It was found that iron, lead and zinc predominated and that the level of iron at times exceeded 10000 μg/l with lead and zinc exceeding 1000 μg/l. Alley and Ellis concluded that the concentrations of trace elements, including various heavy metals were highest during the initial parts of the periods of rainfall runoff and then decreased with time. The instantaneous loads of trace elements were largely a function of the runoff discharge.

Table 4.11 Summary of the quality of rainfall runoff from the Shephall catchment.
(Mance and Harman (1978)).

Wilber and Hunter (1975) in Lodi, New Jersey, found that heavy metal concentrations varied significantly throughout runoff events and from storm to storm. The total heavy metal loadings, average and standard deviations are given in Tables 4.12 and 4.13. In most cases, metal concentration during the rising limb of the hydrograph were typically higher than those during the descending limb, suggesting a first flush effect. Figure 4.2 illustrates the change in flow together with concentration of lead and suspended solids with respect to time over a typical hydrograph. Lead, zinc and sometimes copper were the major contributors of heavy metals in the stormwater runoff examined (for lead, iron, zinc, copper, chromium and nickel). Together these accounted for approximately 90 to 98% of the metals observed. Of this, lead and zinc were found to account for 84% of the total.

Two storms were studied in the Oxhey catchment, Herts., (Morrison et al (1984)) and for all the metals studied, the dissolved phase increased in proportion throughout both storms, and for lead, the dissolved phase became quite significant towards the end of the second storm. Typical road surface sediment heavy metal concentrations (Ellis and Revitt (1982)) indicated that the road surface runoff was the principal source of heavy metals for the two storms. The controlling parameters for the heavy metal partitioning between the dissolved and suspended solid phases were, pH, flow, suspended solids, dissolved organic carbon and dissolved chloride (Morrison et al (1984)).

Figure 4.2 Variation in flow and concentrations of lead and suspended solids for a typical storm hydrograph.
(Wilber & Hunter (1975))

Copper, zinc and cadmium showed secondary and late flushes, suggesting a retarded input of suspended solids enriched with these metals. The late flushes of suspended solid associated metalswere possibly due to the variable contributing source concept. That is, the metal forms have taken longer to arrive from their source, either due to different rates of mobilization or due to the longer travelling distances. These reasons may be further complicated by variations in rainfall intensity over the catchment and some sediments may only be mobilized by heavy and prolonged rainfall (Morrison et al (1984)).

The dissolved metals displayed no initial peak since the metals could have required some time before they became mobilized or required a high rainfall intensity, or they could have been scavenged by the suspended solid phase. The dissolved metals all displayed an increase at the end of the storms, which may be related to the corresponding increase in organic carbon and dissolved chloride. Cadmium was shown to follow the flow both in the dissolved form and within the sediment, which could suggest that cadmium is not controlled by the sediment to the same extent as zinc, lead and copper.

Pollutographs tended to display great variation from one storm to another and between catchments. However, some patterns do emerge and these include the first flush effect, together with secondary and multi-peaks of heavy metals occurring later throughout the flow cycle.

4.8 Stormwater Sediments

The elemental composition and mineralogy of suspended solids in urban stormwater have been investigated by Ellis et al (1981). It was found that the size distribution of particles was strongly bimodal and covered a range of 1 to 50 μm. The elements present in order of decreasing concentration were silicon, aluminium, iron, calcium, phosphorus, sulphur, chloride, potassium, magnesium and titanium. Ellis concluded that stormwater suspended solids were mixtures of materials derived from below and above ground sources, with the mix shifting as contributing sources varied during the stormflow conditions within the catchment. Smaller diameter particles were found to be discharged from the system early in the flow cycle. Subsidary sediment peaks on the recessional limb also tended to be associated with the finer sizes, being primarily derived from surface washoff, for example, the occurrence of the titanium peak late in the stormflow was postulated as being derived from road surface markings. The elemental composition of the solids confirmed that the two major contributory sources to storm drainage pollution was from traffic and the road surface itself (Ellis et al (1981)).

Highway surface sediments and their associated heavy metals may be rapidly mobilized during rainfall activity and washed into a sewer system and subsequently into the receiving water. In a study by Feltz (1980), it was observed that the sediment transported during a storm was almost entirely comprised of fine material less than 0.062 mm. Collins and Ridgway (1980) also reported that at the outlet of a pipe transporting stormwater, more than 90% of the particles were less than 50 microns.

Reinertsen (1981) similarly indicated that the storm runoff entering a street inlet contained less than 10% particles greater than 10 microns in size. The heavy metals have been found to be transported in association with this fine material.

Stormwater solids therefore contain predominantly fine particles which are generally enriched with heavy metals (see Section 5.3.2.3) and Table 4.14, taken from Colwill et al (1984), gives the lead content in different size fractions for both road and runoff sediment. Consequently total metal levels in the suspended solid phase of urban runoff are generally higher than in the corresponding street surface sediments (Morrison et al (1984)).

Revitt et al (1981) studied heavy metal levels in stormwater sediments for three storms in the urban catchment in north-west London. All of the sediment associated metal levels recorded during the stormflow were very high, cadmium was found to reach 670 µg/g during one storm. The results are given in Table 4.15. It is evident from the Table that the values were considerably higher than those previously recorded for raw street sediments within the same catchment (Revitt and Ellis (1980)).

The results indicated that there was considerable metal enrichment occurring within the below ground phase of the stormwater runoff. One explanation given for this enrichment was the depostion of coarser particulate fractions on the recessional limb of the storm events (Wilber and Hunter (1975)), and the requirement of a critical threshold velocity to sccur them from the pipe system. An alternative explanation is that the toxic fines are preferentially washed from the road surface and appear at the outfall as a highly polluted suspended sediment (Ellis and Revitt (1981)).

Between 50 and 75% of heavy metals are held within the carbonate and iron manganes oxide fraction of urban surface particulates (Ellis et al (1982)) and thus may be solubilized relatively easily in the latter phases of runoff. The exchangeable fraction as well as the total extract efficiency decreases in the order Cd > Zn > Cu > Mn > Pb, and is independent of particle size and traffic type or volume, (Ellis and Revitt (1982)). In addition the bacterial mobilization of the organic metal phase of in-pipe sediments can also substantially enrich the soluble levels.

The dissolved phase of urban runoff waters have been shown to contain between 5 and 50% of total heavy metals with the cadmium in particular being very soluble in road runoff. Cadmium, copper and zinc in runoff were found to be present mainly in the dissolved phase, whereas lead was most strongly associated with the suspended solids phase. The pattern of flow weighted metal loadings during storm events indicated that copper, lead and zinc were mainly derived from road runoff, whereas the irregular behaviour of cadmium suggested another source or combination of sources (Morrison et al (1984)).

Recent elemental and textural studies (Ellis et al (1981), (1982)) would suggest that stormwater solids possess relatively short below ground residence and contact times. This would imply that the highly toxic priority pollutants, including heavy metals (being strongly sediment associated) are rapidly routed through the system from both above and below ground sources to the receiving water.

Urban surface dusts and stormwater sediments therefore act as efficient sinks for lead, but not for cadmium, zinc, chromium and copper, which can be preferentially and efficiently desorbed and released into the below ground system. The wide differences in metal extractability also magnifies the dangers of only relating runoff toxicity to source surface sediment concentrations.

Ellis (1979) has also stated that heavy metals can accumulate in the benthal sludges of receiving waters to stormwater runoff, and in organisms, until lethal limits are reached.

In conclusion, therefore, water from road surfaces and sediments may play a significant role in increasing the environmental load of lead, zinc, copper, nickel, chromium and iron (Pope (1980)).

4.9 Stormwater Runoff and Rainfall/Dustfall

A number of workers have compared the heavy metal content found in stormwater runoff to that of rainfall and dustfall for particular areas (e.g. Wilber and Hunter (1975), Horkeby and Malmquist (1977), Dauber et al (1978), Pope (1980) and Randall et al (1978)).

Wilber and Hunter (1975) evaluated and compared the heavy metal loadings in stormwater runoff with those associated with precipitation and secondary treatment plant effluent in Lodi, New Jersey, USA. The distribution of metals in precipitation were found to be similar to the distribution in runoff, with lead and zinc predominating. Due to the high variability in concentrations in the runoff and rainfall, direct comparisons were not feasible. Therefore weighted averages were compared. It was noted that the lead:zinc ratio in precipitation (1.03) was very similar to the lead:zinc ratio in runoff for the same area.

Colston (1974) and Soderlund and Lehtinen (1971) also reported concentrations of lead and zinc, and these ratios can be calculated as 1.3 and 1.66 respectively. This suggests that the origins of lead and zinc in precipitation and runoff may be associated (Wilber and Hunter (1975)). The total annual loads of heavy metals to stormwater runoff were computed in a similar manner to that in the STORM model, the values are given in Table 4.16. Therefore on the basis of these calculations, and within the limits of the accuracy of the data employed, 86% of the total annual load of metals evaluated in the study could be attributable to precipitation.

Many metals, especially iron, zinc and copper display higher concentrations in stormwater than in rain-water (Horkeby and Malmquist (1977)). Horkeby and Malmquist (1977) studied heavy metal concentrations in stormwater and rainfall/dustfall in Göteborg, Sweden, the results are summarized in Table 4.17. From consideration of the Table it can be seen that for arsenic, cadmium, chromium, mercury, vanadium and lead, atmospheric fallout could explain a great deal of the metal content of stormwater. However, for the other metals only a small fraction could be explained by atmospheric fallout. It was concluded from the study that most of the heavy metals originated from traffic and corrosion. However, the samples were taken on only two occasions and therefore the comparisons are somewhat uncertain.

Malmquist and Svensson (1977) carried out a similar study and arrived at similar conclusions. The results of the study are presented in Table 4.18.

It was concluded that the mass flows of zinc and copper in the stormwater could be predicted from atmospheric fallout and corrosion of building materials. However, corrosion explained more of the copper mass flows than the zinc mass flows. Also the mass flow of lead could be explained by traffic volume. The frequency and effectiveness of street sweeping was also found to be important.

Dauber et al (1978) compared the concentration of heavy metals in motorway runoff with those of different effluents and rain-water quality. The results are shown in Table 4.19. Flow weighted mean values for the motorway runoff were significantly higher than those in precipitation, which therefore allowed the conclusions to be drawn that emissions directly caused by traffic contributed substantially to concentrations and mass loads in runoff.

Randall et al (1978) reported the ranges of various heavy metal concentrations found in both rain-water and dustfall. The results are presented in Table 4.20. An inverse relationship was found between the rainfall pollutant concentration and rainfall amount. This indicated that there was a 'first wash' effect i.e. most of the pollutants in the atmosphere were washed out in the initial stages of precipitation and any subsequent rainfall diluted their concentration. When runoff pollutant loads were compared to precipitaion pollutant loads, the latter were found to be higher, which meant that the land surface constituted a net sink for atmospheric pollutants. Dustfall loadings were found to be of a very small fraction of those deposited during precipitation. However, such material would tend to accumulate on the catchment surface, thus adding to the total runoff pollutant load.

Pope (1980) provided a summary, Table 4.23, for the range of heavy metal concentrations found in precipitation, road/street runoff and urban runoff. The numerical values were taken from a number of sources.

In conclusion it would therefore appear that the metal concentrations found in road/street runoff and urban runoff are higher than those in precipitation, except for that of cadmium and in some cases copper. However, despite the proliferation of research undertaken in this field the results display great variability. It would appear that this is mainly due to the nature of the data being both site and time specific. In order to make a 'realistic' comparison it would therefore be necessary to sample the stormwater and rain-water contributing to a specific storm event, although this may not be practicable or feasible in some circumstances.

4.10 Snowmelt Runoff

Very few researchers have studied and compared the concentration of heavy metals in snowmelt runoff with those found in rainfall runoff. This may have been due to the scarcity of snowmelt occasions when sufficient quantity is produced for sampling.

Alley and Ellis (1978) analysed two samples of snowmelt runoff at one site, and these were found to have trace element concentrations equal to or greater than the mean trace element concentrations in rainfall runoff for the same site (Table 4.22). The levels within the snowmelt runoff peaked during the maximum melting period i.e. during the maximum instantaneous runoff period.

Table 4.21 Summary of metal concentrations (mg/l) in precipitation, road/street runoff and urban runoff. (Pope (1980))

Mance and Harman (1978) studied both the rainfall runoff quality and the snowmelt quality for the Shephall catchment. A summary of the results are given in Table 4.23. From consideration of the Table it can be seen that the snowmelt is of poorer quality than the rainfall runoff. The results are comparable with those obtained by Alley and Ellis (1978).

It would therefore appear that snowmelt runoff is of poorer quality, i.e. contains higher concentration of heavy metals, than rainfall runoff. This may be due to a number of factors including the use of road salting chemicals during snowfalls, the less efficient utilization of petrol by motor vehicles and the contact between the snow and the vehicle bodywork.

4.11 Total Annual Loads

The primary objective of many investigations into the problem of heavy metals in stormwater runoff have centered around the prediction of total annual loads exported for a particular catchment.

In Norway, Lindholm and Balmer (1978) estimated the level of annual discharge of pollutants in storm runoff for five separately sewered catchments. The results are given in Table 4.24.

Bryan (1972) estimated that the annual yield of lead from an urban catchment in Durham North Carolina USA to be 0.333 kg/ha/year. Colston and Tafuri (1975) also assessed the annual pollutant yield in urban runoff for a catchment in Durham N C USA, the results are given in Table 4.25.

The annual storm heavy metal pollutant export for one particular catchment, from the EPA study of 13 catchments in Melbourne, Australia, were predicted and can be seen in Table 4.26.

The data from the annual observations display great variability. Each catchment will have individual characteristics, which will effect the heavy metal pollutant loads. It is therefore, difficult to make comparisons between the data since each study is site specific.

The following Chapter is concerned with the source of pollutants to urban stormwater runoff.

CHAPTER 5

SOURCES OF POLLUTION TO URBAN STORMWATER RUNOFF

5.1 Introduction

The eventual pollution load of stormwater runoff is acquired through an accumulation process, the initial stages of which is the contamination of rain-water through contact with various airborne substances. Further collection of pollutants occur as runoff passes over solid surfaces before being finally discharged into the receiving body of water. The relative contributions from the above ground pollutant sources to the total outfall concentrations and loadings remains a speculative and controversial problem.

The pollutants found in urban stormwater discharges would be expected to reflect the path taken by the water as it passed through the atmospheric and urban systems. The potential sources will therefore be discussed under three headings namely, aerial deposition, urban surfaces and below ground.

5.2 Aerial Deposition

The sources of atmospheric pollutants are numerous and varied, correspondingly, the path from the source of emission to the recipient water involves a series of complex processes. The major sources of atmospheric pollution in urban areas include, industrial stacks and vents, construction activities, demolition and excavation projects, agricultural operations, exposed derelict land and vehicular pollution.

Deposition is the removal process through which suspended atmospheric deposits are transferred to surfaces. Deposition processes may take place through three possible mechanisms:

(i) sedimentation, for particles greater than 5 µm,

(ii) surface impaction, for particles smaller than 0.1 µm,

and (iii) wet deposition,

The combination of sedimentation and surface impaction is widely referred to as dry deposition, and can be expressed in terms of deposition velocity. Wet depostion occurs in two modes, washout (below ground processes) and rainout (in cloud scavenging). Bulk deposition includes both wet and dry deposition.

5.2.1 Wet Deposition

Recently growing attention has been given to the concept of 'acid rain'. In recent years there have been many reports of dying lakes, fish kills, sick trees and deteriorating buildings and monuments, which have been attributed to acid rain. However, there are few records to show how it is formed or what sources are specific to acid pollution. Reports have linked acid rain with the oxides of sulphur and nitrogen that are emitted when fossil fuels are burnt during industrial processes and in combustion engines (Kish (1981)). The oxides combine with atmospheric water and vapour to form dilute solutions of sulphuric and nitric acid. It has been shown that acid rain can convert certain harmless substances into toxic forms, the most significant example of which is aluminium (Pearce (1982)).

A number of studies have been carried out on atmospheric pollutants which affect rain-water quality, some of those concerned with metals will now be discussed.

Lazrus et al (1974) collected atmosheric precipitation nationwide in the USA, and was analysed for the heavy metal content of lead, zinc, copper, iron, manganese and nickel. It was found that human activity was the primary source of the metals within the precipitation, and in particular the concentration of lead correlated closely with the amount of petrol consumed within the study area.

The quality of urban rain-water at nine sites in Washington, DC was examined by Randall et al (1978) and the following conclusions were reached:

(i) pollutant quantities in precipitation were of significant magnitude to have a significant impact on the quality of surface water runoff in urban areas,

(ii) the washout of pollutants was relatively uniform across the urban area even though the origin of pollutants may have been area specific,

(iii) atmospheric contaminants were washed out during the first stages of a precipitation event. Thus the resultant loadings on the urban surface from aerial deposition were independent of the magnitude or intensity of precipitation,

(iv) under stable atmospheric conditions the pollutant load within the rainfall increased with the duration of the antecedent dry period,

and (v) the rate of aerial deposition was much greater during precipitation.

5.2.2 Dry Deposition

Some material, normally wind transported 'dustfall', reach the ground without the aid of the stripping or condensation mechanisms of precipitation. Dustfall is a measure of the settleable particulate matter (normally in the range of 20 to 40 microns in diameter), that falls out of the atmosphere under the influence of gravity (Johnson et al (1966)).

Heaney and Sullivan (1971) quoted levels of the average annual dustfall loadings for the Chicago area, USA, as 12900 kg/month/km^2 in 1966. It was estimated that 70% of all material found in the streets of Chicago originated from atmospheric fallout.

Sartor and Boyd (1972) indicated that nutrients and heavy metals in surface runoff waters were significantly influenced by dustfall. Horkeby and Malmquist (1977) also observed for a suburban area in Göteborg, Sweden, atmospheric fallout could explain a high proportion of the arsenic, cadmium, chromium, mercury, vanadium and lead content in the stormwater runoff loadings (see Section 4.9).

Table 5.1, taken from Harrop (1983), is a compilation of recorded data on the contribution of atmospheric fallout, including both rainfall and dustfall, to surface runoff. Very few studies have been undertaken to estimate the contributions of atmospheric pollutants to those found in urban surface runoff.

Mance and Harman (1978) reported that the rate or aerial deposition of pollutants on the Shephall catchment were constant when measured over a period of eight days or more, for shorter periods variations were high. The observed rates of deposition are given in Table 5.2. The rates were found to be within the ranges reported for a national survey by Cawse (1975). Using the measured rate of aerial deposition on the catchment, together with the knowledge of the antecedent dry period and mass discharge in the runoff events studied, it was possible to estimate the proportion of the mass of pollutants in urban runoff that originated from aerial deposition. The proportions are also given in Table 5.2.

5.2.3 Discussion

Research to date shows that generally precipitation and dustfall pollutant concentrations are lower than the average urban runoff concentrations. However, constituent levels indicate that a proportion of most pollutants found in surface water runoff originate from aerial deposition. The actual contributions vary from one locality to another and the eventual contribution will be dependent upon land usage, meteorological and topographical conditions.

Table 5.2 Rates of aerial deposition and the percentage of the mass of pollutants discharged that are derived from aerial deposition. (Mance and Harman (1978))

5.3 Urban Surfaces

Following aerial deposition the next stage in the contamination process takes place whilst stormwater runoff is in contact with urban surfaces, and in particular the road surface.

It has previously been stated that the major contributing factors to stormwater runoff pollution is through the contact with polluted land surfaces. There are two main entry points to the sewer sytem, firstly, from the roofs of buildings direct, since gutters and roof drain pipes are connected directly to the sewer system, and secondly, from the road surface via road gullies.

5.3.1 Roof Surfaces

Roofs represent large impermeable surfaces where deposition of pollutants occur. By virtue of their direct connection to the sewer system, they are a major entry point for stormwater to the sewer system and play a significant role regarding pollution.

Little research has been undertaken on the potential role of roof surfaces as a pollution source. Although it has been shown that aerial deposition is not a significant source of particulate matter, contact with roof surfaces can introduce considerable quantities of suspended solids. Ellis (1977) suggested that between 10 and 30% of the suspended solids loading in the outfall discharge were due to runoff from roofs. This was confirmed by Mance and Harman (1978) who quote 16% for the Shephall catchment. The latter concluded, however, that roof runoff made negligible contributions to the outfall pollutant loadings.

Table 5.3 gives pollutant concentrations in roof runoff discharge. Waller (1972) and Pratt and Adams (1984) have expressed concern that although roof pollutant loadings are generally lower than direct highway contributing sources, they may in some circumstances cause a significant contribution to the eventual loadings discharged to receiving streams and contribute to the first flush of solids in runoff events.

In a recent study by Harrop (1984) it was shown that roof runoff introduced significant levels of pollutants to storm runoff. It was revealed that the roof runoff was a major source of inert solids, reflecting the roof fabric composition of sand and cement. The elevated solids levels, although largely inert in nature, could act as host carriers for other pollutants, cause aesthetic nuisances to streams and blocking of stormwater pipes. The contribution of roof runoff by volume can also be substantial. Harrop (1984) estimated that roof runoff accounted for 4% of the loadings at the outfall pipe.

It has been shown in Scandinavia, where copper and zinc are commonly used as a material for roofing and gutters, that roof and gutter corrosion can generate significant pollutant loadings of these metals. Malmquist and Svensson (1977) state that between 70 and 90% of the total copper discharged, and between 10 and 70% of the zinc, were attributable to roofing materials.

Table 5.3 Pollutant concentration of roof runoff discharge (discharge in mg/l unless otherwise stated).

(1) Waller (1972)
(2) Harrop (1984)

Studies therefore appear to suggest that the composition of solids emitted in the roof runoff reflect the mineralogy of the roof fabric and the contributing atmospheric sources to the roof.

Recently, researchers are becoming increasingly aware that roof runoff is a major source of stormwater pollution, hence refuting the earlier claims that roof runoff made a negligible contribution to outfall pollutant loadings.

5.3.2 Road Surfaces

Meterials present in roadway runoff can originate from a variety of sources (Pope et al 1978), and include:

(i) road surface degradation,
(ii) vehicle lubrication losses,
(iii) vehicle exhaust emissions,
(iv) load losses from vehicles (spillages),
(v) degradation of automobile tyres,
(vi) road surface cleaning and de-icing,
and (vii) rainfall.

The above inputs are illustrated in Figure 5.1, together with the various outputs from the system.

A wide range of studies on pollutants and pollutant levels originating from road surfaces have been undertaken (see Section 4.5). The majority of authors have concluded that street surface runoff is highly contaminated, with most of the pollutants being sediment associated.

5.3.2.1 Composition of Street Surface Contaminants

The composition of material found on street surfaces varies considerably. Although this material is fully mixed, researchers have consistently found the dominant component to be inorganic material similar to sand and silt (Sartor and Boyd (1972), Wanielista et al (1977) and Extence (1978)).

Ellis (1977) found that for the Graham Park catchment, the inorganic material fraction of the street surface sediments accounted for 50 to 80% of the total sample weight. The organic materials proved an extremely variable component but contributed up to one third of the total weight. The rubber and bitumen fractions typically comprised three quarters of all organics (with plant debris 3%, humic fraction 2%, bitumen 4% and rubber 1 to 20% of the total weight (Ellis (1976)). The organic materials were associated with low particle size, with between 15% and 70% associated with particle size less than 0.06 mm.

Ellis (1979) also observed that there was a high proportion of humic and fine solids emanating from residential areas. This was attributed to landscaping and gardening activities.

Prior to the study by Ellis, Tucker (1975) had observed similar characteristics for inorganic particles, and concluded that the impervious surfaces were leached and eroded of their bituminous binding materials, inorganic calcareous grit ($CaCO_3$), cement, sand and ice control salts (NaCl, CaCl and ferrocyanides).

Ellis et al (1981) investigated the elemental composition of the inorganic fraction of stormwater runoff, and found that the solids were dominated by silicon and aluminium. Other elements such as iron, calcium and potassium were present at lower levels, with traces of sulphur, chlorine, phosphorus, magnesium and titanium. The findings correlated well with those of McCrone (1980).

Elemental source tracing of urban dust has been undertaken by Linton et al (1977) and Hopke et al (1980), in the USA. In the later study it was shown that the composition of the roadway dust sample was that presented in Table 5.4.

Organic and oil permeated particles, known as 'black deposits', are also found on road surfaces (Green (1974)) and are generally from the loss of lubricants from moving vehicles. The black deposits have been known to clog tyre treds and obscure road markings (Pope (1980)).

5.3.2.2 Sediment Associated Contaminants and Particle Size

Path and road surface particulate sizes fall within a narrow band width with a large proportion in the fine fraction.

Many pollutants have an affinity for sediments. Sartor and Boyd (1972) observed that a greater proportion of the overall pollution load was located within the fine solids fraction of the street surface contaminants, this is illustrated in Table 5.5. From consideration the Table it can be seen that the very fine silt/clay fraction (less than 43 μm) of the street surface material provides only 5.9% of the total solids loading. However, the finer solids fraction accounts for a quarter of the BOD, one third to a half of the algal nutrients, three quarters of the pesticides and greater than half of the heavy metals.

Ellis (1977) also found that the majority of all pollutants on the road surface were associated with particles less than 200 μm. This particle size range accounted for 25% of the oxygen demand, 30 to 50% of the algal nutrients, 50 to 60% of the grease and rubber, and 30% of the heavy metals were found below 0.06 mm particle size, (although this fraction only accounted for 4-8% of the total street surface sediments). If this size range was extended to 0.2 mm, then 40 to 90% of the pollutants associated with the particulates were included. Correspondingly, Archer and Barratt (1975) observed that the smaller particles of road surface sediments contained the highest concentrations of lead. In a recent study by Harrop (1984) it was also found that there were higher concentrations of heavy metals within the smaller sediment fraction, see Table 5.6.

5.3.2.3 Heavy Metals in Road Surface Sediments

A considerable amount of information now exists confirming the importance of street surface contributions to the heavy metal pollution of stormwater drainage systems (Pitt and Amy (1973), Revitt and Ellis (1980), Ellis and Revitt (1982), Nightingale (1975), and Hedley and Lockley (1975)). It has also been established that aerosols and deposited dusts found in urban areas are substantially enriched with many potentially toxic trace elements, especially heavy metals, by comparison with those in non urban areas (Lee et al (1972) and Rahn (1976)), see Table 5.7. Such dusts may be inhaled following re-entrainment (Rahn and Harrison (1974) and Draftz (1975)), ingested by children (Lepow et al (1974)) or removed to the aquatic environment by runoff following precipitation (Beeton (1975)).

Table 5.6 Mean heavy metal concentrations for road surfaces in Chilwill Gardens against particle size. (Harrop (1984))

Of all the types of dust found in the urban environment, one of those most highly enriched in heavy metals is roadway dust. Lead concentrations have been reported to reach the percentile levels (Solomon and Hartford (1976)), and several other elements, including chromium, manganese, nickel and zinc are also present in disturbingly high levels (Rahn and Harrison (1974)).

Table 5.7 is a compilation of data from various studies indicating the heavy metal concentrations found in roadside dust samples. From consideration of the Table it can be seen that great variability is displayed within the concentrations of heavy metals in road surface sediments. Table 5.8 is a condensed version of Table 5.7 and illustrates the overall ranges and mean values for the various metal concentrations found in urban/residential, motorway and rural environments.

Ellis and Revitt (1982) observed a large variability of individual heavy metal loadings within each road category studied and it was therefore concluded that not all of the heavy metal levels found could be directly related to traffic. The urban metal loads were often seen to exceed those found on motorways, indicating a possible source other than vehicles. This may reflect the composition of the road surface and Shaheen (1975) found that concrete road surfaces yielded higher lead and zinc levels compared to an asphalt surface.

METAL	MIN.	MAX.	MEAN	REFS.*
IRON	1400	128000		1,2,3
			27500	4
		15000		5
			8780	6a
			15280	6b
			23593	22
			21000	2
	13000	43000		2,3
LEAD	128	8300		1,7,8,9,10,11,12
			2110	4
		1500		5
			261	6a
			978	6b
	600	1950		13
			1636	14
	920	3560	1880	12
	150	2330	960	11
			1040	9a
			920	9b
	220	4300	1050	15
			2210	16a
			2760	16b
			2150 - 3460	20
	115	7208	931	21
			124	22
	130	10000		8,15,18,23,24,25
	5	3900		3,7,9,10,12,19
ZINC	13	1110		1,3,12,17,18,19
			464	4
		750		5
			1715	6a
			2133	6b
	200	940	534	12
	10	3270	540	21
			230	22
	44	480		2,17,25
	7.5	710		2,3,12,19
COPPER	25	3170		1,2,3,12
			75	4
		250		5
			35.1	6a
			90.7	6b
	57	312	143	12
	2.73	581.8	136.4	21
			54	22
	22	200		2,25
	33	150		2,3,12

Table continued overleaf

METAL	MIN.	MAX.	MEAN	REFS.*
CHROMIUM	11	91	29	12
			43	4
NICKEL	15	80	35	12
			36	4
			16	22
CADMIUM	0.0034	10.1		3,13,17,18,19
		5		5
			3.6	6a
			6	6b
	1.3	10.1	4.6	12
	0.148	13.6	1.82	21
			1.2	22
	0.22	**2.2**		**17,25**
	0.02	5.4		3,12,19

Table 5.7 Heavy metal concentrations in road surface sediments. (mg/kg)

Key: Urban/Resisential
Motorway
Rural

*

1 Wilber and Hunter (1977)
2 Pitt and Amy (1973)
3 Amy (1974)

4 Wilber and Hunter (1979)
5 Revitt et al (1982)
6 Ellis and Revitt (1982)
a > 250 µm
b < 250 µm
7 Harrison (1976)
8 Smith (1976)
9 Duggan and Williams (1977)
a - Mid urban
b - Outer urban
10 Day et al (1975)
11 Farmer and Lyon (1977)
12 Harrison (1979)
13 Solomon and Hartford (1976)

14 NAS (1972)
15 Archer and Barratt (1976)
16 Colwill et al (1974)
a = 63 - 38 µm
b < 38 µm
17 Lagerwerff and Specht (1970)
18 Pitt and Field (1977)
19 Van Hassel et al (1979)

20 Duggan (1984)
21 Gibson and Farmer (1984)
22 Harrop (1984)

23 Hedley and Lockley (1975)
24 Little and Whiffen (1978)
25 Ward et al (1977)

METAL	MIN.	MAX.	MEAN
IRON	1400 13000	128000 43000	18788 **21000**
LEAD	115 **130** 5	8300 **10000** 3900	1358
ZINC	10 **44** 7.5	3270 **480** 710	136
COPPER	2.73 **22** 33	3170 **200** 150	89
CHROMIUM	11	91	36
NICKEL	15	80	19
CADMIUM	0.0034 **0.22** 0.02	13.26 **2.2** 5.4	3.44

Table 5.8 Summary of heavy metal concentrations in road surface sediments. (mg/kg)

Key: Urban/Residential
Motorway
Rural

5.3.2.4 Pollution Inputs to the Road Surface

5.3.2.4.1 Road Salt

Anti-skid compounds, containing common salt ($Ca\ Cl_2$ and Na Cl) plus specially formulated organic and inorganic compounds, are used for melting ice and to prevent its formation. In addition certain inert material such as sand, ash, grit and cinders, acting as surface abrasives, are used to prevent skidding. However, the use of salt is the most prevalent and therefore has an important impact upon the surface water runoff quality. The rate and frequency of de-icing salt application varies between countries and depends largely on the prevailing weather conditions. The amount of salt added in the UK varies between 14 and 56 g/m^2, depending on conditions. The major pollutants directly derived from de-icing salt are chlorion (chloride ions) and to a lesser extent, ions of sodium.

The addition of salting compounds to streets can cause numerous problems, both to the urban environment and to the receiving stream. Hedley and Lockley (1975) gave the composition of ICI rocksalt and the values are given in Table 5.9. In the study it was found that de-icing rocksalt was a major source of nickel and chromium pollution in urban stormwater runoff.

Hawkins and Judd (1972) found that salting procedures caused chloride levels in excess of 11,000 mg/l in a receiving stream. Bubeck et al (1971) also observed that salt used for de-icing streets near Rochester, New York, had increased the chloride concentration in Irondequiot Bay at least five fold during the past two decades.

Salting does not simply increase the salt and chloride concentration of the receiving water but can also have a secondary effect of causing damage to ornamental vegetation and corrosion of metallic surfaces (Van de Voorde (1973)). Salting on streets can also result in corrosion and enhance the wear of vehicles and street furniture, as well as aiding the breakdown of the road surface by increasing the rate of freeze-thaw cycles.

The addition of rocksalt has also been shown to increase the release of metals from sediments. Pope (1980) acknowledged the fact that the application of de-icing salt may elevate metal levels in the receiving water body. Complexation of mercury and chloride, and competition between sodium and mercury for exchange sites on the sediments is one mechanism which could lead to the increased mobilization of mercury from bottom sediments, as a result of road salt (Feick et al (1972)).

Table 5.9 The composition of ICI Rocksalt.
(Hedley and Lockley (1975))

5.3.2.4.2 Motor Vehicles

Motor vehicles account for approximately 50% by weight of all the pollutants discharged into the atmosphere, transport sources being the greatest contributors to air pollution (Butler (1979)).

Sartor and Boyd (1972) classified the nature of motor vehicle pollution inputs to the road surface as follows:

(i) leakage of fuel, lubricants, hydraulic fluids and coolants,
(ii) fine particles worn off tyres, clutch and brake linings,
(iii) particulate exhaust emissions,
(iv) dirt, rust and coatings under decomposition which fall off the vehicle trim linings, chassis and under carriages,
(v) vehicle components broken by vibration or impact (e.g glass, plastics and metals).

5.3.2.4.2.1 Tyre Wear Products

The wear products from vehicle tyres are potential pollutants to the road surface which have received little attention. Dannis (1974) estimated that the average wear rate per tyre is 90 mg/km, which would mean that in the USA approximately 5 x 10^8 kg of tyre debris are generated each year.

Cadle and Williams (1978) studied tyre emitted pollutants and found that hydrocarbons and sulphur gases were emitted continuously from vehicle tyres under normal wear conditions due to the degradation of polymers. The results indicated that the particles produced were not suspendable and less than 50% of the wear products were airborne particulates.

Christensen and Guinn (1979) reported that the concentration of zinc in urban runoff was quantitatively related to the levels of zinc in vehicle tyres and it was shown that the average zinc deposition onto the road surface was 0.003 gm Zn per vehicle kilometer.

5.3.2.4.2.2 Vehicle Emitted Products

Of all the compounds emitted from vehicle exhausts, lead has been the most widely studied.

Lead in the form of tetra-ethyl and tetra-methyl lead is added as an antiknock agent in petrol. The amount of lead added to petrol varies, but ranges between 0.15 and 0.55 g/l in the UK. A small amount of tetra-ethyl lead is lost by evaporation of the fuel and some will pass through the engine uncombusted. Approximately 75% of the lead in petrol is discharged into the atmosphere and about 20% is retained in the sump oil, the rest is deposited on the inner surface of the engine or exhaust system and subsequently emitted in the form of flakes (Wilson (1982)).

The amount of lead which is discharged from a vehicle engine is dependent upon the rate of acceleration (where 5% is emitted for city driving and up to 2000% with rapid acceleration due to the rapid resuspension of particles in the exhaust system), the traffic density, driving mode and speed, site topography and the prevailing meteorological conditions. Lead concentrations can vary seasonally, it is possible for lead emissions to be doubled during cold operating conditions.

Wilson (1982) suggested that, with the exception of industralized areas, lead from exhaust pipe systems accounted for 90% of the atmospheric lead pollution. During combustion between 25 and 50% of the lead added to the petrol will become airborne in the form of aerosols of lead halides and oxides. As a result it is possible for toxicity levels in city streets to reach 2.4 $\mu g/m^3$, the toxic limit for lead in the atmosphere being 200 $\mu g/m^3$. Numerous researchers have shown the lead content of air to decrease with the distance from a road. Daines et al (1970) found that reductions in the air lead content at 46.2 m from the road surface could show a reduction of 50% of that recorded at 3 m from the road surface. Beyond a distance of 77 m lead concentrations were found to be at normal background levels.

The majority of lead emitted from vehicle exhausts is in the form of particulate inorganic compounds, and normally fall in two distinct particle size ranges of, less than 1 micron in diameter and between 5 and 50 microns, however, a larger size has been found by Habibi (1973) but the former two predominate. The size of particle emitted is a function of the driving mode and speed where high speeds display small particle emission. Particles emitted may be deposited directly to the road surface where they may be partially resuspended and aggregated by the movement of subsequent traffic. Hedley and Lockley (1975) found the deposition of lead to predominantly occur on a 30 m width either side of the road. Colwill et al (1974) also observed a decrease in lead concentration particulate levels with distance from the road. The levels within the soil surrounding the area were also found to decrease with depth, indicating pollution was by deposition.

Chamberlain et al (1979) confirmed the conclusions reached by Colwill et al (1984) and found that lead concentrations within a few meters of a motorway carriage were high (up to 10 $\mu g/m^3$), but rapidly decreased with distance from the road.

Christensen and Guinn (1979) reported that the concentration of lead in urban runoff was quantitatively related to the levels of lead in petrol and, further estimated an average deposition of lead on road surfaces of 0.0049 gm lead/vehcle km.

5.3.2.4.3 Litter and Vegetation

Litter and vegetation are both important pollution sources to the road surface and consequently stormwater runoff pollution. However, their contribution is difficult to quantify due to the considerable temporal and spatial variability in both composition and volume.

Although it may not be an immediate and major source of surface water pollution, litter on streets is important from an aesthetic point of view. The major proportion of litter comprises of packaging material and printed matter. On urban surfaces litter exists both intact and in various degrees of decomposition and may cause blocking of gully pots and storm pipe systems. Sartor and Boyd (1972) analysed samples of road litter and found the presence of dust size fragments of glass and metal. The organic fraction was found to include food and animal wastes and when compared on a weight basis, were generally present in smaller amounts than the dust and dirt fraction. It was also possible for the particulates and organic matter to act as potential 'hosts' for other pollutants such as heavy metals.

Vegetal matter consisting of leaves, pollen, bark, twigs and the associated algal nutrients and pesticides, are either fallen, blown or intentionally dumped onto the urban surface. The volume and composition are functions of season, land use, local landscaping and municipal cleaning practices. Waller (1972) found the nature of material collected to be consistent with the local land use. Pratt and Adams (1981) demonstrated that there was a seasonal variation in street originating organic matter entering roadside gully pots, with a marked increase during the autumn fall period. The problem with vegetative matter is that if it is allowed to accumulate in roadside gully pots it may become resuspended and discharged into the receiving watercourse, where it can cause both a short term oxygen demand and also after sinking to form bottom deposits, can cause a long term oxygen demand (Sartor and Boyd (1972)).

5.3.2.4.4 Spillage

Spillage on road surfaces create pollution problems if they are allowed to be discharged to the receiving watercourse, however, the spillages may be intercepted on the way.

National statistics on accidental spillages of oil, petrol and toxic materials are not available, however, the incidence of them are thought to be relatively infrequent. The Greater London Fire Brigade report an average of approximately 120 chemical incidents a year on roads within the London area, of which the majority are minor petrol spillages (Bickmore and Dutton (1984)). The chemical industries association esitmate that some 200 to 300 road spillages of chemicals occur in the UK each year. However, major incidents occur only 2 or 3 times a year in most Water Authority areas (Bickmore and Dutton (1984)).

The major source of spillages include vehicle transport and misuse and the deposition of materials, such as the disposal of vehicle sump oil into street gully pots. Spillage materials include, dirt, sand, gravel, cement and various bulk and industrial raw materials, such as oil (which is widely transported on roads and hence suseptible to accidental spillage). Deposits of these highly concentrated pollutants as a result of a spillage can have serious effects upon, not only the receiving water quality, but also on the immediate surrounding environment. For example, chemical spills may release certain gases such as chlorine, which can be highly dangerous to persons in the vicinity. Phenols, caustic soda and other chemicals, can pollute nearby streams and rivers, causing difficulties for downstream users. Insecticides endanger birds, fish and other animals. Other chemicals cause fish kills or damage ornamental vegetation, whilst others, such as inflammable gases, are fire and explosion hazards (Harrop (1983)).

Spillages, although they may cause pollution and damage to receiving watercourses, must be regarded as infrequent transient events which cannot be satisfactorily quantified as each is unique in nature.

5.3.2.4.5 Construction Activity

Construction practices can have a varied effect upon the compositional build up of pollutants on urban surfaces. Due to the variety of possible constructional activities any general quantitative analysis of their effect is difficult. Some observations have shown that construction work will increase the levels of road surface mass loadings.

Extence (1978) observed that construction activity on the M1 motorway, caused pollution which 'was serious enough to warrant control measures'. High levels of suspended solids were detected but due to the lower levels of BOD, the solids were considered to be inert in nature. Burton et al (1976) and Extence (1978) found that the result of highway construction was a significant increase in suspended solids in the receiving stream, but no significant increase in dissolved phosphates or nitrogen. Gregory and Walling (1970) and Guy (1970) have shown that there is a marked increase in solids with urban activity.

Bedient et al (1980) revealed that construction sites in Houston, Texas, gave rise to not only high loads of total suspended solids, but also, unlike Burton and Extence, high loads of total phosphorus and nitrogen when compared with a stable fully developed site.

Guy and Ferguson (1962) demonstrated that expanding urbanization activities led to serious sediment deposition in small reservoirs such as Lake Barcroft, Washington, DC, where 25000 tons of sediment were found to be deposited for each square mile of completed residential construction.

Wilson (1984) has summarized the sources of metal contaminants in the motorway environment, which are presented in Table 5.10. The metal content of traffic related materials is given in Table 5.11. Wilson (1984) also stated the percentage composition of traffic related roadway deposits to be: 0.52% rubber, 1.2% lead, 0.008% chromium, 0.012% copper and 0.019% nickel, calculated by weight from measured deposition rates.

Mance and Harman (1978) were able to make an indirect estimate of the rate of accumulation of material on paved and road surfaces for the Shephall catchment. The values presented in Table 5.12 were obtained using the measured rates of aerial deposition, the weathering of the roofs of houses and the rate of accumulation on the whole impervious catchment, deduced from the mass exported by each runoff event. Clearly the input from roads and paved areas was shown to dominate. As a result there is potential for considerable improvement of runoff quality with increased frequency of street cleaning operations.

SOURCE	NATURE OF POLLUTANTS	METAL CONTAMINANTS
Vehicle Associated:		
Exhaust emissions	Gaseous, particulates, carbonaceous materials	Pb (inorganic-particulates), Fe (rust)
Petroleum spillage/ leakage/evaporation	Volatile hydrocarbons	Pb (organo)
Motor oil, transmission fluid, lubricants, antifreeze, hydraulic fluid, undersealant oil sprays	Volatile hydrocarbons, wear metal contaminants, engine oil additives	Pb, Cu, Cr, Zn, Ni, Zn (organo)
Tyre wear	Filler materials, rubber particles	Zn, Pb, Cu, Ni, Cr
Motor vehicle corrosion	Metallic oxides, Vehicle component debris, plastics	Fe, Ni, Cr
Brake lining wear, clutch plate wear	Metal wear products, asbestos	Cu, Ni, Cr, Pb
Roadway Associated:		
Road surface abrasion, road surface filler materials	Mineral grains, rock chippings, bitumen, asphalt, concrete $CaCO_3$	Various
Roadway markings	Paint, rubber	Cr
De-icing salt	NaCl	Various
Litter	Various	Various
External Influences:		
Local geology, area soils, urban developments,	Major mineral components	Various
Industrial emissions	Various	Various

Table 5.10 Sources of metal contaminants in the motorway environment. (Wilson (1984))

Material	Ref.	Metal content (mg/kg)						
		Hg	Ni	Cr	Cu	Pb	Zn	Cd
Gasoline	(a)	0	10	15	4	663	10	(no data)
Lubricating grease		0	0	0	0	0	164	
Motor oil		0	17	0	3	9	1060	
Transmission fluid		0	21	0	0	8	244	
Antifreeze		0	16	0	76	6	14	
Undercoating		0	476	0	0	116	108	
Asphalt pavement		0	1170	357	51	102	164	
Concrete		0	264	93	99	450	417	
Rubber		0	174	182	247	1110	617	
Diesel fuel		0	8	15	8	12	12	
Brake linings		0	7454	2200	30600	1050	124	
Brake fluid		0	31	19	5	7	15	
Cigarettes		0	193	71	716	492	560	
Salt		0	9	2	2	2	1	
Cinders		0	4	0	3	0	7	
Tyre Rubber:	(b)	(no data)						
Dunlop SP						1.4	13300	1.9
Goodyear G800						0.5	9200	0.15
Pirelli Cinturato						1.0	11800	1.5
Kleber V10						48	8600	6.7
Diesel Fuel:								
Esso Autodiesel						3.7	14.8	0.15
Lubricating Oil:								
Esso Extra 20/50						0.5	635	0.05
Shell 20/50						0.5	825	0.10
Castrol GTX						0.5	900	0.48
Duckhams 'Q'						0.5	1120	0.10
'Used' Oil:								
Duckhams 'Q' *						1380	1120	0.12
Garage bulk storage tank						2800	1060	0.41

Table 5.11 Metal content of traffic-related 'pure materials'. (Wilson (1984))

* used in Volkswagen K70 vehicle for 5000 km

(a) after Shaheen (1975)

(b) after Williams et al (1973)

Average rate of accumulation on impervious area (mg/m^{2}d)	Rate of accumulation on roads and paved areas (mg/m^{2}d)	Rate of aerial deposition (mg/m^{2}d)	Rate of decay of roofing material (mg/m^{2}d)	Input per rainfall event (mg/m^2)
104.5	148.8	26.1	16.7	55.5

Table 5.12 Estimates for the rate of accumulation of particulate matter on the catchment.
(Mance and Harman (1978))

5.4 Below Ground Sources of Pollution

5.4.1 Gully Pots

Gully pots, also referred to as catchbasins and catchpits, are below drain chambers placed along the roadside to act as inlet points for rain-water and stormwater runoff to the sewerage system. The principal purpose of gully pots is to remove solid material transported by the runoff which may subsequently cause sewer blockage. The water seal which is formed prevents the release of bad odours from the sewer and also acts as a reservoir of warmth to help keep the inlet from freezing during severe weather conditions.

Several studies in the UK (Fletcher et al (1978), Mance and Harman (1978) and Waller (1972)) and abroad (Sartor and Boyd (1972) and Cordery (1976)) have suggested that the water stored in gully pots may present a significant source of pollution itself.

In simulated tests carried out by Sartor and Boyd (1972), gully pots were found to be relatively ineffective at preventing pollutant material washed from the streets from entering the sewer system before being discharged into the receiving watercourse. The gully pots were shown to collect large quantities of organic matter and after a period of decomposition, the resultant liquors were flushed out during storms as slug loadings. However, Cordery (1976) in Sydney, Australia, observed reductions in the concentrations of suspended solids, BOD and phosphates as 79%, 34% and 57% respectively, as a result of settling. Waller (1972) sampled the liquids in gully pots during storm events and during the passage of a surface runoff hydrograph, where there was evidence of a deterioration in observed quality. However, the samples were taken in the vicinity of the surface of the liquor and may not therefore have been representative of the whole pot.

Within the Shephall catchment there were 656 gully pots all containing an estimated 100 $m^3$of poor quality water (Mance and Harman (1978)), which was a significant volume when compared with the mean volume of 363 m^3 of runoff water discharged in the events studied. The mean water quality from four pots were monitored for a period in excess of one year and the results are summarized in Table 5.13.

Fletcher et al (1978)) have described the sequence of events leading to the deterioration of gully pot liquor quality. Generally, the poor quality water in gully pots is replaced during rainfall events by oxygenated water, which is relatively low in bacteria but carries a polluted sediment load. At the end of each rainfall event the suspended solids in the gully pot settle out. Bacteria on the walls of the pot, in the sediment and in suspension, rapidly grow in the replenished nutrient conditions, and exert an oxygen demand in addition to any COD carried with the runoff water. The growing bacteria form thick surface scums, which physically support subsequent dry dustfall and invade the water column. Dissolved oxygen is rapidly exhausted (usually within 24 hours) at a rate depending upon the magnitude of the previous rainfall and area of road to be drained. As the dissolved oxygen levels decline, bacterial reduction of nitrates causes a transient increase in nitrite and permanent increase in ammonia, the concentration of which is related to the duration of the antecedent dry period. The increases in ammonia and BOD are confined to the warmer summer and autumn period, low winter temperatures inhibiting bacterial activity. The next rainfall event will cause the surface scum and anoxic water to be flushed out into the sewer system, and in separate systems this could represent a considerable portion of the initial pollutant load.

POLLUTANTS		1	2	3	4	5	6
BOD	Min.	-	-	-	2.3	-	-
	Mean	-	13.7	241.3	-	-	160
	Max.	-	41.6	1500	-	-	-
Suspended solids	Min.	-	-	-	0	-	-
	Mean	71	35	-	-	-	-
	Max.	1032	252.8	-	-	5427	305
Soluble solids	Mean	282	143.2	-	-	-	-
	Max.	5860	292.5	-	-	5360	-
Total solids	Mean	353	-	-	-	-	-
	Max.	5964	-	-	-	8739	-
Chloride	Min.	-	-	-	6.4	-	-
	Mean	76	18.2	-	-	-	-
	Max.	1829	36	-	31525	-	-
Soluble organic carbon	Mean	29	-	-	-	-	-
	Max.	255	-	-	-	-	-
Ammonia N	Mean	0.7	1.39	-	-	-	-
	Max.	4.5	4.62	-	-	-	-
Nitrate N	Mean	0.08	9.6	-	-	-	-
	Max.	0.34	28	-	-	-	-
Nitrite N	Mean	0.8	-	-	-	-	-
	Max.	3	-	-	-	-	-
Phosphates	Mean	-	-	0.2	-	-	-
	Max.	-	-	0.3	-	-	-
Total copper	Mean	0.02	-	-	-	-	-
	Max.	0.04	-	-	-	-	-
Total manganese	Mean	0.2	-	-	-	-	-
	Max.	0.62	-	-	-	-	-
Total lead	Mean	0.17	-	-	-	-	-
	Max.	0.6	-	-	-	-	-
Total nitrogen	Min.	-	-	-	42.2	-	-
	Mean	-	-	12.23	-	-	-
	Max.	-	-	33.2	965	-	-
COD	Mean	-	67.3	6589	-	-	-
	Max.	-	428.6	37700	-	-	-
pH	Mean	-	7.87	-	-	-	-
	Max.	-	8.38	-	-	8.5	-
Total zinc	Mean	0.11	0.09	-	-	-	-
	Max.	0.25	0.57	-	-	-	-
Turbidity (NTU)	Max.	-	-	-	-	125	-
Conductivity (umhos/cm)	Max.	-	-	-	-	9350	-
Volatile sus. solids	Max.	-	-	-	-	385	-

Table 5.13 Gully pot liquor concentrations (mg/l). (Harrop (1983))

1 Water Research Centre (1977)
Mance and Harman (1978)
2 Fletcher et al (1978)
3 Sartor and Boyd (1972)
4 Tucker (1975)
5 Harrop (1982)
(unpublished data)
6 Waller (1972)

At high rainfall intensities, flow through the gully pot may be sufficient to cause resuspension of the fine sediments, further increasing the pollutant loads.

As a result of studies on gully pot liquor quality, Fletcher et al (1978) concluded that there were a large number of variables which determined the quality of stored water in any one gully pot and the effect of any one source of pollution. The following conclusions were drawn:

(i) the most important climatic influence affecting the quality of gully pot liquors was in the summer dry periods, which resulted in sharp increases in the BOD, COD, ammonia and dissolved solid values,

(ii) the loss of dissolved oxygen and the consequent anaerobic conditions were possibly the major cause of pollution,

(iii) over dry periods, human activity in the vicinity of a gully pot caused a significant deterioration of the pot liquor quality,

(iv) human activity led to variation in quality between gully pots,

(v) COD values for the liquor appeared to be dependent upon human activity/catchment area. BOD appeared to be unaffected,

(vi) dissolved oxygen levels were related to catchment area. The introduction of wider spacing between gully pots would increase average dissloved oxygen levels and hence reduce pollution of runoff to gully liquors,

(vii) comparison of pollutant runoff curves and values of certain parameters in gully pots provided an indication of the principal origin of pollutants,

(viii) gully pots were efficient in the removal of heavier particulates from the stormwater runoff.

Mance and Harman (1978) also noted that, during a period of dry weather, significant changes in the water quality within the gully pots occurred. Ammonia concentration increased as oxidized nitrogen was reduced by bacteria. At the same time the total concentration of heavy metals increased, possibly indicating bacterial mobilization of the metals from the bottom sediments. Figure 5.2 records the mean change in concentration of heavy metals in a gully pot in relation to the occurrence of rainfall. This change in concentration was dependent upon the concentration of metals before the rainfall occurred. If the initial concentration was high then a decrease in concentration always occurred. When the initial concentration was low an increase in concentration occurred. It was suggested that this was probably due to the gully pots having submerged outlets with low flowrates where vertical mixing was poor and poorer quality runoff water displaced the cleaner gully pot water, before it was itself discharged. Also during dry periods the gully pot water evaporated and this provided a small volume of storage, which at low rainfall would restrict or even prevent discharge from the gully pot and could also lead to an increase in the concentration of pollutants.

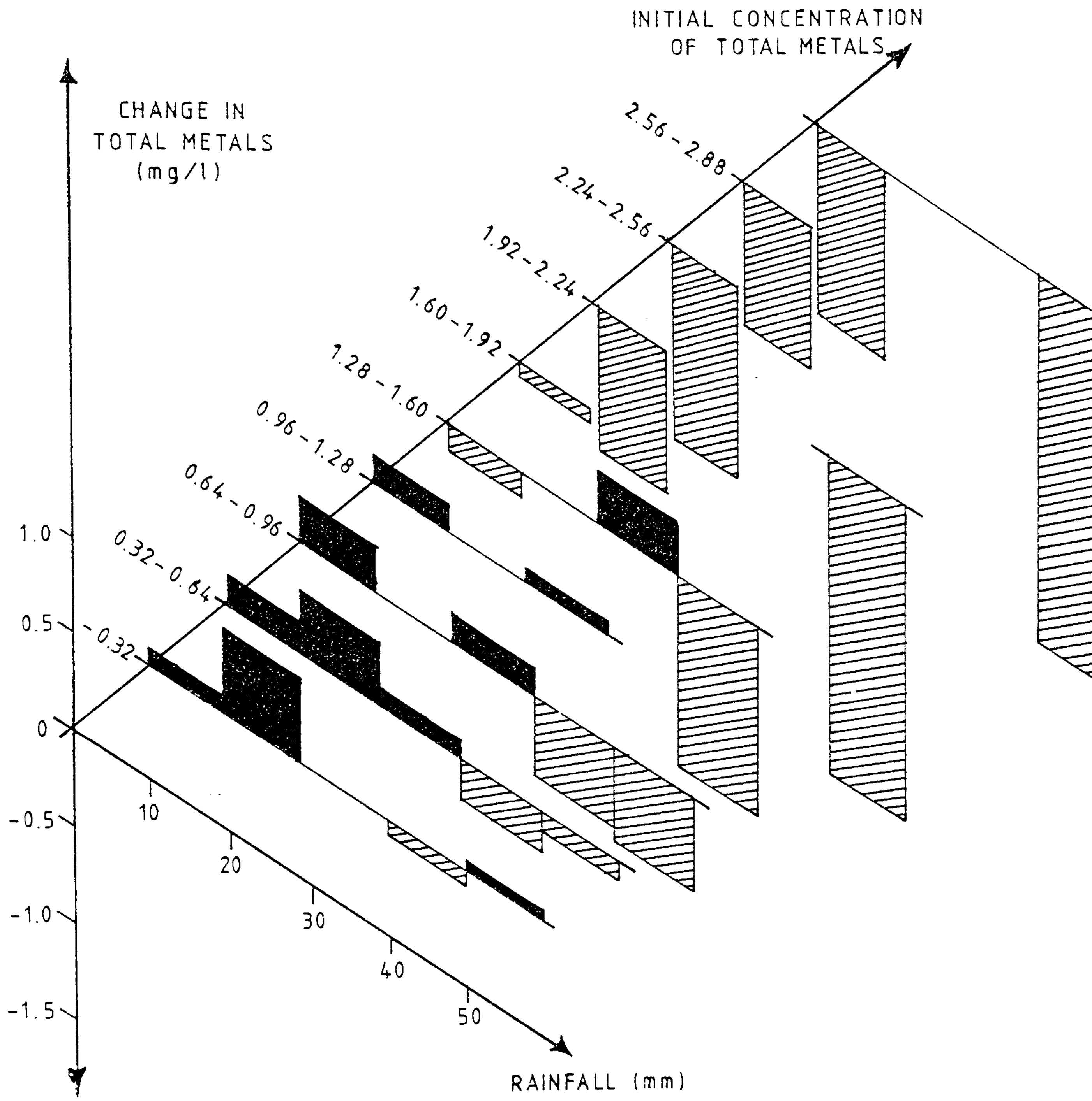


Figure 5.2 Mean change in concentration of heavy metals in gully pot water in relation to rainfall and initial concentration. (Mance and Harman (1978))

Similar patterns were observed for all constituents, with the exception of oxidized nitrogen for which rainfall caused an increase in concentration (Mance and Harman (1978)). In the study, grab samples were also taken to determine the quality of water within the gully pot, before and after rainfall events. It was indicated that the effects of these reservoirs on the mass flow of particulate matter through the system was variable. At times, gully pots trapped an estimated mass of particulate solids equivalent to 50% of the total mass discharged, whilst for other events as much as 20% of the mass discharged may have originated from gully pot waters.

Fletcher and Pratt (1981) concluded that the percentage load contribution of pollutants from gully pots was high, and obtained mean percentage values which were; suspended solids 10.6%, dissolved solids 20.7%, COD 20.5%, BOD 13.9%, nitrate 15.7% and ammonia 31.5%. It was also found that the contribution of contaminants from gully pots were greater after 10 days of dry weather and for the majority of storms the suspended solids were derived from solids already suspended and not from resuspended material from the gully pot bottom.

Harrop (1983) has collated the findings from a number of research studies and these were summarized in Table 5.13.

5.4.2 In-Pipe Deposition

The only data available on the effects of solids deposited in sewer systems are those provided by Gameson and Davidson (1963), for a combined sewer system. Mance (1981) unfortunately found that there was no information available on the occurrence of this phenomena in separate sewer systems.

By controlled flushing of sewers with clean water the accumulation of solids in a pipe system was measured at Northampton by Gameson and Davidson (1963). The estimated rate of deposition distributed over the whole sewer system was approximately 15 gm of solids per metre of sewer per day, i.e. approximately 30% of the dry weather load was deposited within the sewer system during dry weather. This estimate agreed with the rate of deposition predicted by a regression equation developed in the USA for inclusion in the Stormwater Management Model (Pisano and Queiroz (1977)).

$$T_S = 0.024\ L^{1.063}\ \bar{s}^{0.4375}\ q^{-0.51} \qquad (5.1)$$

where: T_S is the total solid loads deposited (kg/day),

L is the length of the sewer (m),

$\bar{s}$ is the mean pipe gradient,

q is the daily discharge per capita ($1p^{-1}d^{-1}$).

Values for Northampton of, $L = 15590$, $\bar{s} = 0.013$, $l = 153$, produced an estimated rate of deposition of 24.8 g $m^{-1}day^{-1}$ compared with the measured value of 15 g $m^{-1}day^{-1}$.

5.4.3 Discussion

It has been demonstrated in this Chapter that the composition of water discharged from a storm sewerage system differs from that of the surface runoff entering the system because of the effects of solids deposited and scoured from the gully pots and sewers, plus the contributions of any roofs that are directly connected to the sewer system.

There is little doubt that gully pot storage and in-pipe biochemical digestion produce anoxic conditions and toxic products which can provide a substantial, if variable, portion of BOD, COD, ammonical nitrogen and fine solids loadings during storm discharges (Tucker and Mortimer (1978), Fletcher et al (1978) and Mance and Harman (1978)). The resuspension of fine solids from both gully pots and sewer pipes also actively mobilizes sediment associated pollutants and flushes them through the system. However, recent elemental and textural studies suggest that stormwater solids possess relatively short below ground residence and contact times (Ellis et al (1981) and (1982)). This implies that highly toxic priority pollutants such as trace metals and hydrocarbons, which are strongly sediment associated, are rapidly routed through the system from both above and below ground sources to the receiving stream. This does not mean that end of pipe first flush management would substantially reduce the problem of stormwater runoff quality, as only 40 to 60% of the total loadings are contained within the time of concentration, and some flushes occur very late during the storm event.

It may be concluded that gully pots, although effective as traps for larger particles and debris, may themselves be a significant source of contamination for separate stormwater sewers.

5.5 Concluding remarks regarding heavy metals

5.5.1 Wet and Dry Deposition

Significant quantities of heavy metals have been reported in urban rain-water (Malmquist and Svensson (1977) and Cawse (1974)) and urban traffic contributes large quantities of lead and other heavy metals to the immediate environment (Harrison et al (1981)). It has been shown that even in relatively unpolluted areas, rainfall and dry dustfall may be a major contributing source of heavy metals in stormwater runoff (Randall et al (1978)).

5.5.2 Urban Surfaces

This non-point source makes an important contribution of heavy metals to urban runoff. Vehicles have been conclusively identified as one of the major contributors (Newton et al (1974) and Bryan (1974)). Christensen and Guinn (1979) reported the average deposition rates of zinc and lead on road surfaces to be, 0.0030 gm Zn/veh km and 0.0049 gm Pb/veh km respectively. An accumulation on the road surface between storms is to be expected, with the rate of metal build up being related to traffic density and type, duration of antecedent dry period and the season. The urban surfaces convey these pollutants effectively to the sewer system and hence to the receiving watercourse during a rainfall event. In Scandinavia, copper and zinc are commonly used in roofing and guttering and their corrosion may generate large amounts of these metals (Malmquist and Svensson (1977)).

5.5.3 Sub Surface Deposition

This category includes in-pipe deposition and gully pot accumulation deposits. According to Mance (1981) in-pipe sediments generally accumulate at a mean rate of 17.15 g sediment per metre per day, and metals may accumulate at a proportional rate. Harrop et al (1983) have reported greatly enhanced levels of heavy metals in gully pot sediments, particularly in the finer fractions. There is evidence to suggest that elevated levels of metals occur in gully pot sediments over and above those which are characteristic of the road surface, this is particularly noticeable in the finer size fractions (Harrop (1983)).

CHAPTER 6

FACTORS INFLUENCING STORMWATER QUALITY

6.1 Introduction

The previous Chapter, Chapter 5 identified various pollution sources to stormwater runoff. The extent and polluting potential of these sources at any given location are governed by a number of factors which include the following:

(i) catchment characteristics, the area and slope of the land, the percentage of impervious areas connected to the surface water sewers, soil type, the number of road gullies, and in particular the road surfaces themselves,

(ii) municipal cleaning practices,

(iii) land use, including, the number and density of buildings, the population of inhabitants, the number of vehicles, the presence and nature of industry, aerial emissions, the type of cultivation of unpaved areas and the tree and vegetation cover,

The above factors determine the nature and polluting potential within any catchment. The extent to which this potential is realized during a given storm event is governed by a number of forces (Tucker (1975)) including:

(i) weather patterns, temperature, wind speed, wind direction and the length of the antecedent dry period,

(ii) seasonal variations, the effect on the activity of organisms and the production of wastes (e.g. autumn leaf fall, insect and animal deaths),

(iii) time of day, the effect of human activity and other activities e.g. traffic movements,

(iv) precipitation characteristics, intensity and duration,

(v) runoff characteristics, the effect of rate of flow and time during the storm.

6.2 The Road Surface

One of the main entry points direct to the sewer system is the road surface, the mechanisms controlling contaminant levels on the road surface are therefore of prime importance to any surface water runoff quality study. The continual mass input of contaminants to the road surface is balanced by periodic washing of the surface by rainfall and cleaning procedures.

6.2.1 Deposition and Accumulation

Prior to the entrainment and transport of particles on the road surface, complex accumulation and depositional patterns of the surface materials occur. The accumulation of surface material is determined by the deposition and removal rate, which can be related by a simple storage equation thus:

$$\text{Accumulation rate} = \text{Deposition rate} - \text{Removal rate} \qquad (6.1)$$

The deposition rate is a function of the characteristics of the area e.g. atmospheric inputs, land use, traffic and street surface conditions. The removal rate is a function of street cleaning procedures, deflation, traffic and rainfall, all of which are intermittent events.

6.2.2 Removal of Contaminants

Sartor and Boyd (1972) found that the removal of material from a unit area of street was proportional to the material accumulated and the intensity of the specific rainfall event.

The efficiency with which the rainfall removes contaminants from surfaces is dependent upon a number of factors, including, rainfall intensity, duration, size of droplets and the impaction rate. A simple exponential relationship between surface loading and rainfall can be used to describe the removal of surface contaminants, which has been used by Sartor and Boyd (1972), Sylvester and De Walle (1972) and Singh (1974) and is as follows:

$$Li - Lt = Li\,(1 - e^{-KR}) \qquad (6.2)$$

where: Li and Lt are the initial surface loading and after time t respectively (mg/m^2),

R is the cumulative rainfall up to time t (mm),

K is the removal constant (mm^{-1}).

The removal constant K reflects the ease of removal of the contaminants. It is high for soluble surface contaminants (i.e. are easily removed). K is approximately 1.8 mm^{-1} for sodium de-icing salt (Laxen (1975)) and 0.1 for suspended sediment (Sylvester and De Walle (1972)). In the former case a 90% removal of surface contaminants occurs after 2 to 3 mm of rainfall, but more than 20 mm of rainfall is required for the removal of suspended solids.

6.2.3 Surface Distribution of Contaminants

The spatial distribution of particles on the road surface is not uniform, but highly skewed, with an estimated 90% occurring within 150 mm of the kerb (Mance (1982) whose findings agree with those of Ellis (1977) and Sartor and Boyd (1972)). The greatest metal loadings within road surface sediments has been shown to occur in the gutter and on the kerbside (Hamilton et al (1984)).

Roadside kerbing stones are a major factor influencing the accumulation and removal of sediment associated surface contaminants. Graham et al (1974) noticed that the length and height of the kerb prevented solids from being transported from the road surface to adjacent areas, and hence, accumulation of solids occurred in the gutter zone. However, Reinertsen (1981) demonstrated that although approximately one third of the total mass of contaminants on the roadside were deposited next to the kerb, only 10 to 20% of these pollutants were added to the water as it travelled down the gutter.

Pratt (1984) studied the usefulness of kerbing stones, from a pollution point of view, in the UK. It was concluded that the kerb stones actually aided the accumulation of road surface sediments and dust etc., therefore their usefulness from a pollution control viewpoint was debatable.

6.2.4 Surface Characteristics

The characteristics of the road surface itself may influence the contaminant levels found there, and these have been investigated by Sartor and Boyd (1972) and Peterson and Gupta (1978). Both studies found that the layout of the street surface could influence the accumulation rate of contaminants and provide storage/retention areas for surface pollutants.

Both highway and path surfaces possess surface depressions, which largely account for the observed spatial anomalies of surface sediments. The accumulation of fine polluted fractions within the surface depressions, between storm events, inevitably induces toxic levels of heavy metals which will impose considerable stress upon the stormwater system during eventual storm flushing conditions (Revitt and Ellis (1980)).

The road construction material can contribute to the sources of pollutant materials through their breakdown products, but may also influence the entrainment and cross surface transport of pollutant associated sediment.

The type of road construction material used was shown to directly effect the runoff quality. According to Sartor and Boyd (1972) asphalted street surfaces have 65% greater pollutant loadings than those of concrete, and in addition pavements in poor condition had pollutant loadings between 2 and 2.5 times greater than that on new pavements. A study on the M1 motorway near Watford Gap (Green (1974)), confirmed these findings and it was observed that loadings on asphalted surfaces were often 60 to 80% higher than those on adjacent surfaces.

6.3 Municipal Cleaning Practices

Municipal cleaning practices are intended to remove road surface particulates and their associated pollutants in order to reduce the aesthetic nuisance of surface litter and to minimise the problem of pollutant loadings to the receiving watercourse. Municipal cleaning practices vary from one area to another, but may include one or more of the following direct or indirect methods (Harrop (1983)).

(a) Direct methods:
  (i) street cleaning,
  (ii) gully pot cleaning,
  (iii) refuse and litter collection,
  (iv) sewer flushing,
  (v) snow and ice control.

(b) Indirect methods:
  (i) street surface maintenance,
  (ii) air pollution controls,
  (iii) open air maintenance,
  (iv) construction,
  (v) motor vehicle parking regulations.

Recent studies have criticized the effectiveness of various cleaning procedures. Numerous workers, including Sartor and Boyd (1972), Pitt (1979) and Ellis (1979) have come to some general conclusions on street cleaning procedures.

(i) They are effective in removing litter and vegetation. There is almost a total removal of particulate matter greater than 10 mm with a 50% removal for particles of 1 to 10 mm and only 15 to 20% removal for particles less than 0.06 mm (Ellis (1979) for the Graham Park Catchment).

(ii) Multiple runs of street sweeping over the same area reduce the particle loading on the street. Sartor and Boyd (1972) observed that a second run removed approximately 50% of the remaining residue. However, multiple sweeping of the same section in the Graham Park catchment (Ellis (1979)) did not increase removal efficiency.

(iii) There is an inverse relationship between the effectiveness of various motorised road sweepers and vehicle speed.

(iv) Following the application of any road sweeping method there is a redistribution of sediment across the road surface. Prior to cleaning, the greatest concentration is nearest the kerbside, after cleaning, the residue not collected is redistributed over the outer road surface.

Motorised road sweepers are less efficient than manual ones, and vacuuming is the most effective procedure. In a review by Mance (1981) it was noted that manual sweeping caused a significant reduction in particles greater than 0.1 mm, whilst vacuum cleaning was effective down to 0.06 mm. However, none of these methods caused a significant reduction in particles smaller than 0.06 mm in size. Hydrojetting is another cleaning technique but is not usually employed in the UK. Swedish research has indicated that it is extremely effective in removing a wide range of particle sizes, including the fines. However, it only moves the water quality problem from the above ground phase to the below ground system.

In order to obtain maximum removal of pollutants the sweeper must be operating at its maximum efficiency and this is dependent upon a number of factors including the age, texture, diameter and rotational speed of the sweeping broom and on the operators performance and competance. The cleaning efficiency is also dependent upon the type of surface and its condition. Poor quality road surfaces with cracks and surface irregularities cause difficulty in the sweeping operations, leaf deposition causes the clogging of gully pot inlet gratings and snowfall generally impedes street cleaning procedures.

Serious obstructions are caused by parked and abandoned vehicles which act as a barrier to cleaning procedures and often cause particulates to resettle towards the centre of the road. Pitt (1979) and Levis (1974) observed that accumulation of materials occurred beneath cars with a gradual decline in the quantity of deposited particles towards the front and rear of the vehicle. As vehicles prevent the sweepers from getting close to the kerb, their effectiveness is reduced. The only remedy to this problem is the application of stricter parking restrictions during cleaning periods.

The removal of road surface particulates is not only dependent upon the equipment type and use, but also upon particle size and the spatial distribution of particulate loadings over the road surface. Sartor and Boyd (1972) and Pitt (1979) carried out extensive studies on the effect of sweeping procedures upon particle size distribution and composition. It was noted that the overall removal effectiveness of surface particulates was approximately 50%, although the prime effect of cleaning was to cause a redistribution and shift in grain size predominance (Sartor and Boyd (1972)).

Prior to cleaning there was a predominance of the middle size fractions, whereas after cleaning the smaller fraction predominated, the larger size ranges having decreased markedly. The removal rates for the larger particles were found to be greater than 70%, with an insignificant removal of the percentage of finer, contaminated related solids. Table 6.1 summarizes the findings for the removal efficiency rates of various particle sizes. The removal efficiency for the litter fraction was often found to be between 95 and 100%. Ellis (1979) confirmed these findings and showed that mechanical sweeping, the most commonly used method in the UK, removed only some 15 to 20% of particles less than 0.06 mm.

As the major proportion of pollutants are associated with the finer particles of less than or equal to 0.2 mm, it would seem that street sweeping procedures are ineffective in reducing the end of pipe loads in urban runoff pollution (Sartor and Gaboury (1984)). Even if mechanical sweeping was 100% effective for particle sizes down to 1 mm, the pollution loading would only be reduced by approximately 20%.

Gully pot cleaning is required to prevent the formation of pollutant gully pot liquors from being discharged into the pipe system during periods of runoff. Eductor or clam shell buckets are the most common methods employed to clean gully pots, where the supernatant liquid is effectively removed. However, the main problem is to ensure that a regular programme is followed as sporadic cleaning is of little use. Within the UK gully pots are only usually cleaned once or twice per year, irrespective of season or local circumstances. Regular gully pot cleaning together with dry weather in-pipe flushing would lead to a more effective means of surface water quality control.

Particle Size microns	Sweeping Efficiency %
> 2000	79
840 - 2000	66
246 - 840	60
104 - 246	48
43 - 104	20
< 43	15

Table 6.1 Sweeping removal efficiency for individual particle size ranges. (Sartor and Boyd (1972))

6.4 Land Use

The immediate and surrounding land use is of crucial importance when studying the surface runoff quality from any catchment. The three widely accepted land use categories are residential, industrial and commercial.

Sartor and Boyd (1972) noticed considerable variations in pollutant concentrations between land use categories. Streets in industrialized areas tended to be more heavily polluted than those in residential areas, and commercial streets were the least heavily loaded. When comparing the loadings in runoff from a variety of sites in Halifax, USA, Waller (1972) found that the solid loadings were highest for the commercial areas, whereas BOD and coliform concentrations were highest for residential areas. The studies of Wanielista et al (1977) revealed that there were lower concentrations of suspended solids, nitrate and phosphate, but higher organic pollutants, in residential areas when compared with runoff from commercial areas. Similarly, Barkdoll (1977) noted that phosphates were greater in residential and suburban areas when compared with runoff from urban areas.

The results of a study by Melanen (1977) are presented in Table 6.2. From consideration of the Table it can be seen that the runoff from industrial areas is the most heavily polluted followed by the traffic category, with the residential areas providing the least pollution.

	AREA		
	Residential	Industrial	Traffic
Total dry solids	83 - 740	2022	300 - 1140
Volatile dry solids	4 - 157	572	70 - 170
Suspended solids	37 - 700	1150 - 1460	110 - 1300
Volatile suspended solids	17 - 190	250 - 276	42 - 200
Settleable solids (2 hours)	0.4 - 3.5	4	-
pH	4.99 - 7.26	7.25 - 7.61	6.12 - 8.05
Conductivity (mS/m)	1.2 - 10.8	8.4 - 9.2	5.4 - 27.2
Chlorides	0.3 - 9.5	4.3 - 9.2	2.1 - 20
Sulphates	1.0 - 21.5	8.2 - 12	6.0 - 40
Lead (µg/l)	16 - 770	365 - 380	415
Oil	0.4 - 1.6	-	19 - 42

Table 6.2 Urban runoff quality variations over the 1977 experimental period in the Finnish Stormwater Project.
(Melanen (1977))

Note concentrations in mg/l unless otherwise stated.

Housing density has also been seen to effect runoff quality. Whipple et al (1978) indicated that for multiple family housing areas, the concentration of heavy metals, BOD, ammonia and phosphate were greater within the runoff than for an area consisting of mainly low density housing. The findings were only partially in agreement with those found by Polls and Lanyon (1980).

6.5 Antecedent Weather Conditions

It is reasonable to postulate that pollutants accumulate on the urban surfaces in the catchment between rainfall events, and that the quality of water discharged by any runoff event will be related to the length of the preceeding dry period.

Considerable amount of doubt has been expressed concerning the postulation that the antecedent dry period has a significant influence on surface runoff contaminants (Mance and Harman (1978), Whipple et al (1977) and Bedient et al (1980)). The view that there is some influencing effect exerted by the length of the antecedent dry period has been emphasized by the use of this parameter in the Stormwater Management Model (SWMM (1971)).

Sartor and Boyd (1972) noted that the longer the dry period, the greater the build up of inorganic materials on catchment surfaces, and concluded that it was an important factor affecting pollution loads originating from road surfaces.

In an early study at the Oxhey catchment (Wilkinson (1956)), an increase in the average concentration of BOD and PV (Permanganate Value) in the early part of storms was identified, as the duration of the antecedent dry weather increased. However, no such relationship was discernable for suspended solids. In contrast, Tucker (1975) did observe a relationship between the mass of suspended solids and the length of the antecedent dry period.

The pollutant concentrations found in gully pots have also been attributed to the varying length of the antecedent dry period. Fletcher et al (1978) correlated the sharp rises in BOD, COD, nitrate, ammonia and total dissolved solids in gully pot liquors to antecedent dry weather conditions. A correlation, with a correlation coefficient of 0.85, was also observed between antecedent dry weather conditions and both ammonia and total dissolved solids.

Many of the researchers who agree on the importance or significance of the antecedent dry period do so primarily on the basis of studying BOD, a parameter regarded as being an unsuitable indicator for urban stormwater pollution by Colston (1974) due to the BOD test being unsatisfactory in the presence of high concentrations of toxic substances that are found within such runoff.

Contrary to these findings, various researchers have found no evidence to support the concept that the antecedent dry weather period has any effect on the surface runoff quality.

Adams (1978) found that the mean concentration of the total suspended solid loads were not related to the length of the antecedent dry period. However, the peak concentrations of suspended solids were seen to correlate reasonably well with the dry period. No effect in the variations of the 1 to 7 day dry periods on the initial BOD or sulphate values in surface runoff were found by Warnock (1970). Waller (1972) suggested that the scatter of plotted data, plus poor correlations, made it difficult to interpret if there was any relationship between the antecedent dry period and the strength of pollutants in the surface runoff. It was also noticed that municipal cleaning practices, vehicles, the resulting deflation and anthropogenic activity, had a masking effect which also affected the results.

Clearly the evidence to date indicates that the rate of accumulation of pollutants on the urban catchment will be related to the activity during the antecedent dry period as well as its duration, the season of the year and the magnitude of the previous and current rainfall events.

There is considerable contradiction and confusion in the literature regarding the importance of the antecedent conditions on pollutant runoff levels. Many workers would agree that the antecedent dry period correlates weakly with both metal and solid concentrations in runoff, and Harrop (1983) concluded that it was more of a contributing factor to the deterioration of surface water quality, than a major influencing factor on pollutant concentrations in runoff.

6.6 Seasonal Variations

The contaminant loadings found in urban stormwater runoff are influenced by seasonal weather and biological cycles. Seasonal weather cycles may influence individual contaminants due to the effect of rainfall patterns, dispersion of aerial contaminants (e.g. smog and mist), temperature variations, the cumulative effect of organic matter on natural degradation processes, and the erosion of runoff surfaces. The seasonal biological cycles include the effects upon the activity of bacterial organisms, the production of wastes (e.g. leaf fall, insect and animal deaths), the effect of cleaning and scavenging practices, which include the removal of air pollutants by vegetation, faecal breakdown by insects and the general dietary and scavenging habits of animals (Tucker (1975)).

Much conjecture exists within the literature concerning the influence of yearly seasonal environmental patterns upon the build up of contaminant loadings and the quality of stormwater runoff. Weibel et al (1964) found no pronounced seasonal variation in the composition of runoff in Cinncinnatti, Ohio, USA.

The AVCO (1970) concluded that the season with the greatest amount of runoff produced the largest pollutant levels. Droste and Hart (1975) found seasonal variations in the suspended solids, BOD, coliforms, nutrients, nitrates and orthophosphates, and demonstrated that higher values of these parameters were found in the spring and summer. It was postulated that this might have been due to the mixture of weather patterns and human and land use activity within the catchment. Seasonal variations in BOD and nitrate levels were found by Whipple et al (1974), with higher levels occurring in August. Burm et al (1966) noted higher solids loads during the spring within the stormwater runoff, but the BOD values did not vary appreciably throughout the year.

Waller (1972) has shown seasonal variations in solids, BOD, bacterial counts, chlorides and phenols. Tables 6.3 and 6.4 show the results. Apart from the evidently higher solids and chloride levels in the winter and higher phenols during the fall, no clear pattern was evident due to the limited number of samples taken. Dauber et al (1978) also found higher chloride levels during the winter months and Waller (1972) concluded that these higher levels were related to the use of de-icing salt. A tendency for a build up of suspended solids levels from road salting operations has also been shown by Hawkins and Judd (1972).

Rossano and Johnson (1966) observed a seasonal variation in dustfall, with maximum values occuring in March, April and May. During the rest of the year the levels were relatively constant. It was therefore postulated that the urban stormwater runoff would reflect these variations. However, the effects may have been masked by local land use and municipal cleaning practices.

The time of the day may also have an influencing factor upon the surface runoff pollution, however, this may be more prevalent within a combined sewer system. Gameson and Davidson (1963) found that storm sewage was the weakest during the middle of the night, at which time the dry weather flow was at a minimum and the crude sewage, weakest.

Average Concentration	sample	Jan - Mar	Apr - June	July - Sept	Oct - Dec
Suspended solids (mg/l)	C Q	327 (3) 645 (2)	191 (4) 147 (169)	54 (146) 131 (152)	66 (30) 104 (82)
Volatile suspended solids (mg/l)	C Q	100 (3) 107 (2)	79 (4) 39 (169)	15 (146) 57 (152)	22 (30) 36 (82)
BOD (mg/l)	C Q	- -	- 29 (24)	52 (11) 32 (10)	36 (17) 19 (26)
Coliform (per 100 ml)	C Q	- -	- -	7.0E6 (20) 4.6E6 (15)	0.17E6 (5) 3.3E6 (8)
Fecal coliform (per 100 ml)	C Q	- -	- -	11.0E3 (20) 15.0E3 (15)	7.3E3 (5) 2.3E3 (8)
Fecal strep. (per 100 ml)	C Q	- -	- -	23.0E3 (20) 27.0E3 (15)	4.0E3 (5) 30.0E3 (8)

Table 6.3 Seasonal variation in composition of surface runoff at Cambridge Street and Quinpool Road.
(Waller (1972))

(number of samples shown in parentheses)

C - Cambridge Street
Q - Quinpool Road

23.0E6 = 23×10^6

	Year	Month									
		A	M	J	J	A	S	O	N	D	J
Chloride (mg/l)	1969		6								
	1970		14		14		13			786	
Phenol (mg/l)	1969				60						
	1970	38			23			99			

Table 6.4 Median seasonal values found by Waller (1972) for chlorides and phenols at various sites.

For a separate stormwater sewer, the time of day may also influence the quality of runoff by affecting human activity within the catchment, such as traffic numbers and road maintenance practices, for example, the majority of road salting operations were performed after 6 pm or before 8 am, when the roads were least busy.

Although not all studies on urban stormwater runoff have observed seasonal variation in runoff quality, it would seem apparent that the runoff pollution levels would exhibit some seasonal variations, even though they may be slight. Many may be masked by other influencing factors, hence any direct seasonal variation would be difficult to interpret.

6.7 Precipitation Characteristics

It is clear from the literature that the duration, volume and intensity of rainfall are prime factors in determining the quantity of material removed and transported by surface runoff.

The contribution of rainfall characteristics, such as intensity, volume and duration, to the pollution loads in urban stormwater runoff have been studied by a number of researchers, including Pravoshinsky and Gatillo (1969), AVCO (1970), Sartor and Boyd (1972), Waller (1972), and Harrop (1984), many of which have stressed the relationship between rainfall intensity and the load produced.

Using multiple regression analysis, AVCO (1970) suggested that precipitation variables were the most significant in predicting runoff quality in Tulsa, USA. Work by Adams (1978) confirmed these conclusions.

Reinertsen (1981) observed that a single rainstorm event alone dramatically reduced the contaminant levels on street and paved surfaces. In addition many high intensity rainfall events, following each other, brought about a reduction in the contaminants of approximately 80% over a one and a half month period.

The effective rainfall has also been found to be a major influencing factor on the outfall loadings for particular catchments (Kidd (1978)).

Defillippi and Shih (1971) observed a logarithmic relationship between total rainfall and the load per storm of BOD and COD. A similar relationship for total solids and to a lesser extent BOD was found by Hergert (1972), who in addition noted a variation with rainfall intensity. Lazaro (1979) and Soderlund et al (1972) have also stressed the correlation between rainfall intensity and load.

Dauber et al (1978) found that, with the exception of chlorides, all mass loads were distributed throughout the year according to the total amount of rainfall. In a recent study by Harrop (1984) both total and organic solids loadings removed from the road surface correlated strongly with the recorded rainfall volumes. These findings agreed with the slightly earlier studies by Pratt and Adams (1981). This relationship between rainfall volume and the loads produced has also been observed by Waller (1972), Pope (1980), AVCO (1970) and Adams (1978). Reinertsen (1981) noted that the concentration of contaminants in stormwater runoff were volume dependent during the first 1.8 to 2.1 mm of rainfall excess, but no volume or time dependence was observed thereafter.

6.8 Runoff Characteristics

The correlations between total storm loadings and runoff concentrations to the runoff characteristics have also been studied by a number of researchers.

Weibel (1964) found evidence of a strong correlation between the concentration of pollutants in surface runoff and the rate of discharge. Conversely, Wilkinson (1956) noted the absence of any correlation, but found that for many storms, peak flow and peak pollutant concentration coincided.

Many workers have demonstrated first-order linear relationships between metal loadings, total solids and storm runoff volume (e.g. Whipple et al (1978) and Bourcier and Sharma (1980) , although, Pope et al (1978 b) stressed that it was the peak flow intensity rather than the volume which was significant in runoff terms. However, total runoff volume has been found to correlate well with total pollutant loads (Bedient et al (1980), Mance (1981) and Ellis (1982)). It has been suggested that runoff volume was the most significant factor in predicting stormwater runoff pollutant concentrations and loadings. Total pollutant loads have also been seen to correlate well with both the maximum amd mean flowrates (Harrop (1984)).

The runoff volume and maximum runoff intensity are therefore the major influencing variables on the mechanisms of contaminant removal from surfaces.

Variations of pollutant concentrations occur within a storm as it proceeds. As the flow of surface runoff increases so does the scour of the solids, whereas increased flows cause greater dilution of the components within the runoff. As time proceeds during a storm event, pollutant concentrations tend to decrease due to the progressive effects of scouring (Waller (1972)).

Waller (1972) found that both the suspended solids and bacterial concentrations decreased with time from the begining of the storm. It was concluded that higher rates of discharge yielded higher solids concentrations and bacterial densities decreased with the rate of flow, presumably because of the effects of dilution exceeded those of scour. Warnock (1970) also found a decrease in concentration of BOD, solids and sulphates during the storms and Miche and Dhamadhikan (1971) found a similar relationship with turbidity, which decreased after the begining of the storm.

Work carried out by Colston (1974) using regression analysis, showed that the rate of runoff and the time from the start of the storm accounted for 73 to 94% of the explained variance of nineteen quality variables.

Studies undertaken have therefore shown that discharged concentrations and loadings can be strongly related to both rainfall and runoff characteristics. They play an important role in the transportation of pollutants from the urban surfaces to the stormwater sewer. However, transport is only achieved when the critical threshold is exceeded by rainfall inputs to generate overland flow and thus effect pollutant mobility.

CHAPTER 7

THE EXPERIMENTAL CATCHMENT

7.1 Introduction

A residential urban catchment at Chelmsley Wood in north-east Birmingham, with a completely separate sewer system, was the subject of the field investigation. This chapter will describe the site, its location and the various sampling and measuring systems employed to monitor the pollution load at the outfall of the stormwater sewer. To assist in defining the pathways followed by the heavy metal pollutants, a network of deposit cannisters and a programme for sampling soil and roadside dust was established. Meteorological data were obtained by on site measurements and from nearby meteorological stations. Additional data, including road salting and road cleansing records were obtained from the Solihull District Council. A traffic survey was also undertaken in order to estimate the number of vehicle kilometers travelled per day, within the catchment.

Figure 7.1 shows the various contributing sources of pollution to the urban stormwater runoff system, and how they were monitored at the Chelmsley Wood site. The sampling period ran from July 1983 to July 1984.

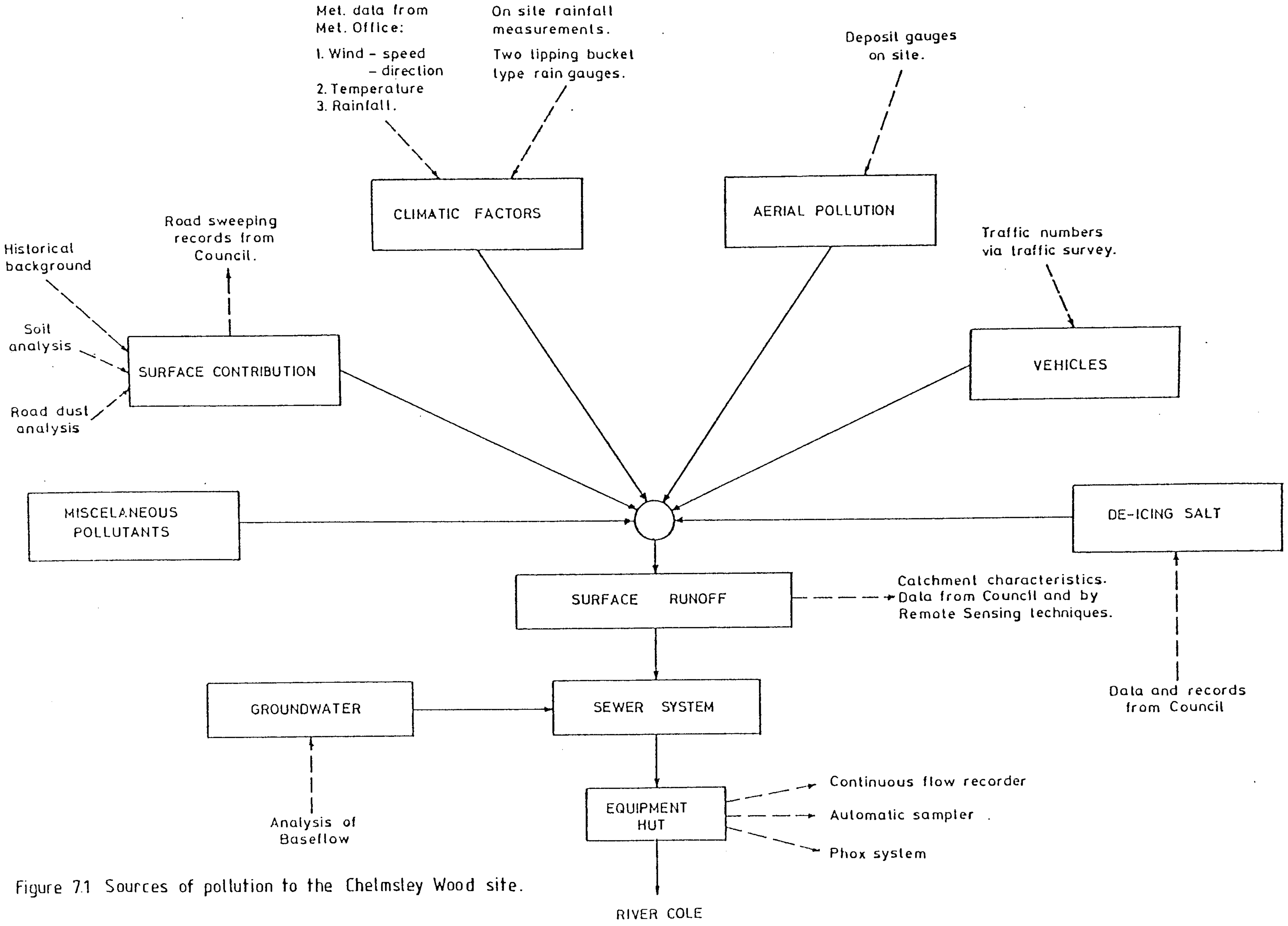


Figure 7.1 Sources of pollution to the Chelmsley Wood site.

7.2 The Catchment

The experimental catchment was situated in Chelmsley Wood, Solihull, West Midlands, approximately 17 km to the north-east of Birmingham city centre. The national grid reference for the area was SP/174 893.

The area of Chelmsley Wood studied was almost entirely a residential council estate, whose occupancy was predominantly that of tenants. Within the experimental catchment there were approximately 3200 dwellings with an estimated population of 11500. The estate was constructed between 1965 and 1969 and incorporated a totally separate sewer system. It was because of the recent construction of the estate that it was selected for study, since it was most likely that there was little possibility that the separate stormwater sewer system had been corrupted by either direct connections of foul water or seepage from the system.

The properties within the experimental catchment were mainly low rise buildings, interspersed with some high rise blocks of flats. The style of housing was very uniform and the properties were mainly semi-detatched or terraced. Within the less desirable areas, much of the housing was of low standard, whereas in other areas, especially around the perimeter, were of much higher standard. There was no industry within the area, but a small shopping centre was located in the southern part of the catchment, with additional local shops scattered throughtout the area. There were three main schools together with a couple of newly constructed old peoples homes. Much of the surrounding area was open land.

A large feeder road passed around the northern and eastern perimeter of the catchment, and parallel to this was the M6 motorway, see Figure 7.2. All road surfaces within the area were of Tarmacadum.

Prior to construction, the area was agricultural land with some woodland. Site investigations revealed that the geology of the area consisted of Keuper Marl, with between 350 and 650 mm of topsoil underlain by silty clay and clayey silt, with inclusions of sand and siltstone. The groundwater over the site occurred generally at shallow depths, between ground level and 1.2 m. Chemical analysis of the soil and groundwater samples showed them to be near neutral pH and of low soluble sulphate concentration. No records of metal analyses were taken, at that time.

The catchment characteristics have been determined from aerial photographs, from WMCC Cartographical Services, 1980 (see Plate 7.1), and from the use of remote sensing techniques with the aid of a computerized digitizer.

The total experimental catchment area was 107 hectares (ha), of which 39 ha were impervious surfaces (roads 15 % and roofs 22%). All the roofs and roads drained directly to the separate storm sewer system.

The general layout of the sewer system is presented in Figure 7.2. All the sewers were in good condition and on visual inspection were found to be self cleansing. A dendritic pattern of stormwater drainage pipes was evident with bore size ranging from 225 mm to 1.4 m in diameter. The total length of pipes within the area was 1155 m with a total of 244 separate pipes. The total lengths and number of pipes for each diameter size is given in Table 7.1.

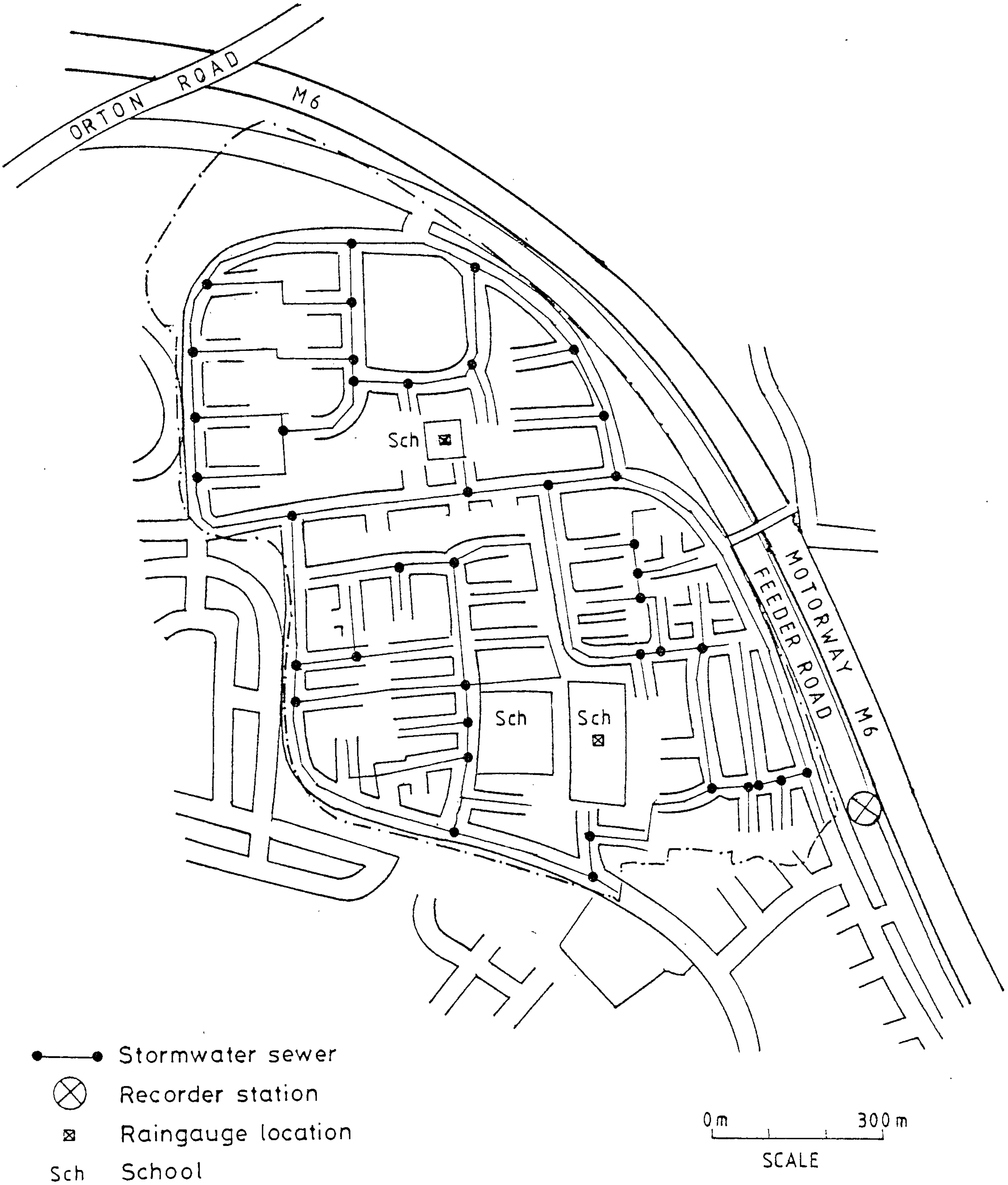


Figure 7.2 The Chelmsley Wood catchment showing stormwater sewer, raingauge locations and recorder station.

Plate 7.1 Aerial photograph of Chelmsley Wood catchment. (WMCC Cartographical Services (1980))

Pipe diameter (mm)	Length (m)	Number of pipes
225	321	119
300	151	42
375	130.5	29
450	49	9
525	6	1
600	58	8
750	126	14
112.5	216	16
135	97	6

Table 7.1 Length and number of pipes of a given diameter for the Chelmsley Wood site.

The catchment area fell in the direction of drainage, with an average gradient of 1 in 220. The gradient of individual pipes displayed variation and Table 7.2 gives the number of pipes with a specific gradient.

Once the stormwater sewer left the experimental catchment it passed under both the A 452 feeder road and the M6 motorway. Approximately 300 m to the north-east of the motorway, the sewer discharged into an open channel, where it was joined by other outfalls. It then ran for approximately 800 m through open fields before its confluence with the River Cole. This is shown in Figure 7.3.

Experimental work at the Chelmsley Wood site was initiated by Birmingham City Council in 1978 in an attempt to assess the impact of stormwater pollutant loadings on the receiving waters and to contribute to the debate on the merits, or otherwise, of separate as opposed to combined sewerage systems.

Early work at the Chelmsley Wood site has been documented by Mance (1981) and an earlier study by Smith (1979). However, since that time , little work has been carried out, apart from flow and rainfall monitoring, until the current research project. The site was instrumented in order to monitor rainfall, runoff and stormwater runoff quality. The monitoring system established at that time, provided the basis of the network used in this study.

Gradient	Number of pipes	Percentage of total
< 1:10	8	3.28
< 1:20	13	5.33
< 1:30	24	9.8
< 1:40	35	14.34
< 1:50	23	9.43
< 1:60	21	8.6
< 1:70	7	2.87
< 1:80	19	7.79
< 1:90	11	4.5
< 1:100	19	7.79
< 1:110	12	4.92
< 1:120	14	5.74
< 1:130	6	2.46
< 1:140	6	2.46
< 1:150	2	0.82
< 1:200	12	4.92
< 1:400	7	2.87
< 1:700	5	2.05

Table 7.2 Number of pipes with a specific gradient for the Chelmsley Wood site.

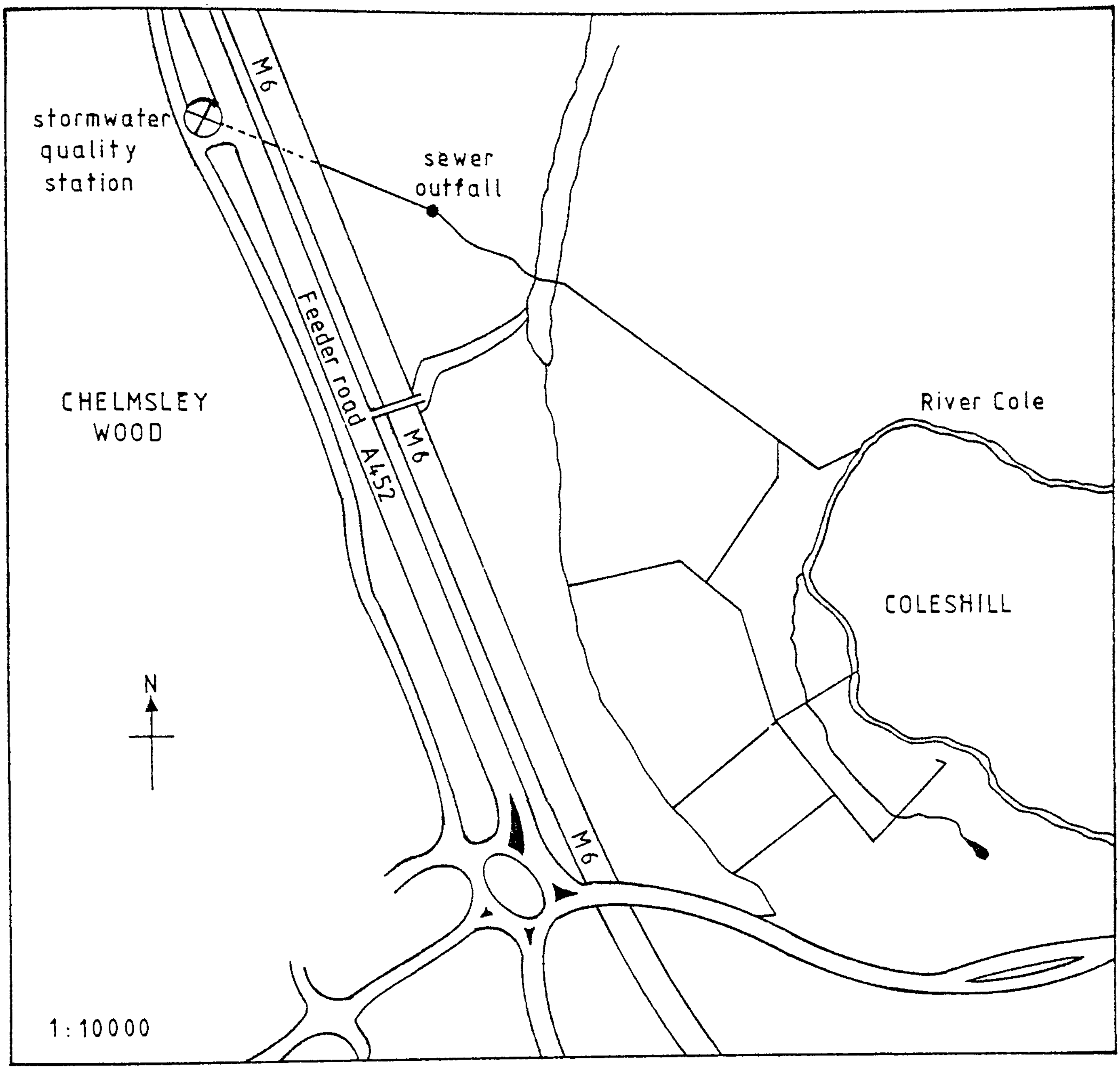


Figure 7.3 Location of the Chelmsley Wood stormwater sewer outfall.

7.3 Instrumentation

Throughout the study, two tipping bucket type raingauges were located within the catchment area (see Figure 7.2), measuring rainfall in increments of 0.2 mm. The rainfall measurements were recorded onto a data logger and the tapes later deciphered by Birmingham City Council. Additional meteorological data, including wind speeds and directions, temperature, relative humidity and sunshine hours were obtained from the meteorological offices at Elmdon Airport, approximately 6 km to the south of the study area, and at Birmingham University.

Stormwater samples, flow data and continuous water quality measurements (using the Phox instrument) were collected at the recorder station, situated above a manhole on the 1.4 m diameter outfall sewer, at a point where it left the catchment, see Figure 7.2.

Since the study area was almost entirely residential, with no direct industrial contributions, it was assumed that the pollution inputs to the sewerage system, were limited to normal suburban activities, aerial deposition and vehicular activity. In order to quantify the inputs and to assess the pathways of individual pollutants from their source to the sewer, it was deemed necessary to look at both landborne and airborne sources of pollutants. A network of deposit cannisters was therefore established and roadside sediment samples were taken at the same locations (see Chapters 9 and 10). Soil samples were also taken at random locations throughout the catchment, as near as possible to the deposit cannister and roadside sediment locations, (see Chapter 11).

All samples collected were analysed for the same seven heavy metals, i.e. iron, lead, zinc, copper, chromium, nickel and cadmium. The reasons why these heavy metals were selected was due to several factors including the concern due to their high potential toxicity, the ease of analytical procedure, practicability and the ability to compare the results to similar studies.

The various instrumentation and analytical techniques employed in acquiring these data sets are discussed in greater detail in Chapter 8.

Road maintenance records for the study area were obtained from Solihull District Council. Road salting commenced during the week beginning 21 November, 1983 and terminated in the week beginning 5 March, 1984, thus covering a 16 week period. The amount of salt used (i.e. the rate of spread) was stipulated in the WMCC Code of Practice for Winter Maintenance, and was given as follows:

(i) precautionary salting 20 gm/m^2,
(ii) light spread 20 to 40 gm/m^2,
(iii) heavy snow 40 gm/m^2.

Only in severe conditions did the rate of spread exceed 40 gm/m^2. Main roads, such as link roads, through roads and bus routes, known as priority routes, were always treated each time a warning was given. Figure 7.4 shows the priority routes for the Chelmsley Wood site. None of the interior roads were treated unless complaints were received and footpaths along the priority routes were only treated in severe conditions. The priority routes made up approximately 40% of the total road area.

Figure 7.4 Road salting priority routes in the Chelmsley Wood catchment (Solihull District Council).

The dates, times and rates of spread of salt, throughout the sampling period are given in Table 7.3. The type of salt used by the WMCC was neat ground rock salt, grade 4, supplied by ICI, and was the same as that which was analysed by Hedley and Lockley (1975) (see Section 5.3.2.4.1).

Street cleaning within the area consisted of both mechanical and manual techniques. The through roads, for example, Aukland Drive, Lanchester Way and Windward Way, were mechanically swept approximately once every two weeks. Cul de sacs were swept by smaller machines approximately once every twelve weeks and footpaths were cleaned manually by mobile crews once every eight to ten weeks. The mobile crews consisted of two to three men who worked around the area on a cyclic basis. There were three types of cleanse:

(i) litter pick,
(ii) medium cleanse (i.e. litter pick and swept if necessary),
(iii) thorough cleanse (i.e. litter pick, swept and cutting back of vegation etc.). This is only usually carried out once every year.

Litter picking at the front of shops and public buildings occurred daily and bins were emptied at the same time. Gully pots were usually emptied four times a year. The type and amount cleaning performed was dependent upon the time of year and associated activities (e.g. leaf fall and school holidays). The sediment and debris collected during cleaning were removed and tipped at a local dumping site. The dates and locations of the various cleaning events which were carried out during the sampling period are given in Table 7.4.

DATE	TIME (24 hr)	RATE OF SPREAD (gm/m^2)
29/11/83	0500	20 - 40
	1800	20 - 40
05/12/83	0500	20 - 40
11/12/83	0500	40
12/12/83	0500	20 - 40
	1800	20 - 40
03/01/84	0500	20 - 40
	1800	20 - 40
04/01/84	0500	20 - 40
09/01/84	0500	20 - 40
12/01/84	0500	20 - 40
14/01/84	0500	20 - 40
15/01/84	0500	20 - 40
17/01/84	1800	20 - 40
19/01/84	0500	20 - 40
20/01/84	0500	20 - 40
22/01/84	0500	40
	1800	40
23/01/84	0500	40
	1800	40
24/01/84	0500	40
	1800	40
26/01/84	0500	20 - 40
30/01/84	0500	20 - 40
31/01/84	0500	20 - 40
01/02/84	0500	20 - 40
05/02/84	0500	20 - 40
09/02/84	0500	20 - 40
13/02/84	0500	20 - 40
	1800	20 - 40
15/02/84	0500	20 - 40
21/02/84	0500	20 - 40
	25 Number of days on which Salting occurred	40 Average Salting rate

Table 7.3 Road salting records for the Chelmsley Wood site during the sampling period July 1983 to July 1984.

(Records taken from Solihull District Council)

Lanchester Way	Aukland Drive	Tamar/Kingfisher Drive	Usk Way
	R O A D S		
02/06/83	02/06/83	24/06/83	16/06/83
22/06/83	22/06/83	31/08/83	29/07/83
06/07/83	06/07/83	29/09/83	29/02/84
04/08/83	03/08/83	21/10/83	
24/08/83	24/08/83	01/11/83	
13/09/83	13/09/83	06/12/83	
27/09/83	27/09/83	04/01/84	
11/10/83	11/10/83	20/02/84	
25/10/83	25/10/83	21/03/84	
17/11/83	17/11/83	19/04/84	
30/11/83	29/11/83	17/05/84	
16/12/83	15/12/83	15/06/84	
19/01/84	30/12/83	17/07/84	
17/02/84	18/01/84		
29/02/84	10/02/84		
14/03/84	28/02/84		
28/03/84	14/03/84		
11/04/84	28/03/84		
30/04/84	10/04/84		
09/05/84	24/04/84		
22/05/84	09/05/84		
05/06/84	22/05/84		
19/06/84	05/06/84		
05/07/84	19/06/84		
	03/07/84		
	P A V E M E N T S		
08/06/83			09/06/83
06/07/83			14/07/83
22/08/83			25/08/83
17/11/83			29/09/83
12/01/84			17/01/84
15/02/84			17/02/84
08/03/84			12/03/84
02/04/84			04/04/84
02/05/84			09/05/84
04/06/84			06/06/84
			17/07/84
	G U L L Y	P O T S	
18/11/83	27/07/83	15/08/83	
14/02/84	18/11/83	23/11/83	
	10/02/84	15/02/84	

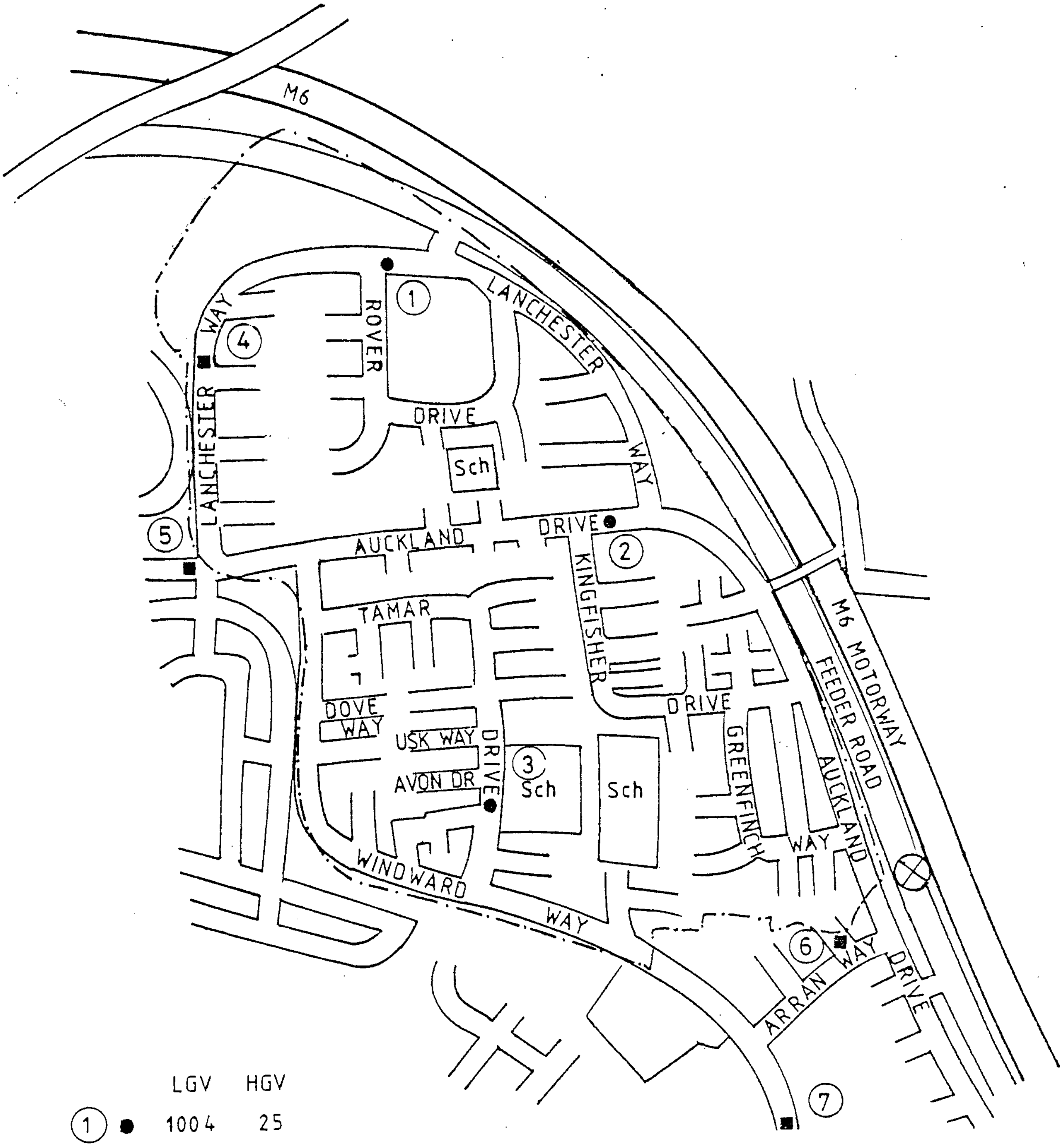
Table 7.4 Street cleaning records for roads, pavements and gully pots for the Chelmsley Wood site.

No other road maintenance activities (e.g. resurfacing) were carried out during the sampling period. Sewer maintenance facilities are performed as and when necessary, and none were recorded during the sampling period.

Within the literature it was found that vehicles were a major source of metals to the road surface (see Section 5.3.2.4.2). A traffic survey was therefore undertaken in order to assess the number of vehicles within the catchment during a specified time period. The total number of vehicle kilometers travelled within the catchment was also calculated, since it was reasoned that this would give an indication of the various metal inputs direct to the road surface.

Traffic figures were obtained by manual counting for a twelve hour period at three locations within the catchment, see Figure 7.5. The values obtained were then extrapolated using data from the WMCC, (based on a 100 point census, which gave the percentage of yearly traffic flow in each week) to obtain weekly traffic flows throughout the year. Table 7.5 shows the weekly figures for (a) the total number of vehicles within the catchment and (b) the total vehicle kilometers travelled. Additional traffic data were obtained from the WMCC for locations in and around the area. These were automatic counts taken over a twelve hour period. The number of vehicles passing a given location in twelve hours for both the authors study and from the Council's data are included in Figure 7.5. As can be seen the Council's data are consistent with the authors study and has therefore been taken as verification of the findings.

The traffic survey also revealed that the contribution from commercial vehicles was negligible, private cars predominated with motor cycles providing a small presence.



		LGV	HGV
①	●	1004	25
②	●	1744	217
③	●	645	7
④	■	766	28
⑤	■	1641	132
⑥	■	668	115
⑦	■	997	88

● study data

■ council data

Figure 7.5 Vehicles passing given locations in a twelve hour period (study and council data).

Table 7.5 Weekly traffic flow data for the Chelmsley Wood Site.

LGV = Light Goods Vehicles
MC = Motor Cycles
HGV = Heavy Goods Vehicles (including buses)

Total traffic flow in catchment
Total vehicle kilometers (Veh Km)

(Data taken from WMCC)

Week No.	% Yearly flow	LGV		MC		HGV	
1	1.72	95599	9095	3336	314	9571	912
2	1.90	105604	10047	3685	347	10572	1008
3	1.91	106159	10010	3704	349	10628	1013
4	1.93	107271	10206	3743	353	10739	1024
5	1.89	105048	9994	3666	345	10516	1003
6	1.80	100046	9518	3491	329	10016	955
7	1.85	102825	9783	3588	338	10294	981
8	1.88	104492	9941	3646	344	10461	997
9	1.95	108383	10311	3782	356	10850	1035
10	1.99	110606	10523	3859	364	11073	1056
11	1.99	110606	10523	3859	364	11073	1056
12	1.97	109494	10417	3821	360	10962	1045
13	1.95	108383	10311	3782	356	10850	1035
14	1.55	86510	8196	3006	283	8625	822
15	1.99	110606	10523	3859	364	11073	1056
16	2.01	111717	10629	3898	367	11184	1066
17	2.06	114497	10893	3995	376	11462	1093
18	1.96	108938	10364	3801	358	10906	1040
19	2.07	115052	10946	4015	378	11518	1098
20	2.03	112829	10734	3937	371	11295	1077
21	2.02	112273	10681	3918	369	11239	1072
22	1.57	87262	8302	3045	287	8736	833
23	2.01	111717	10629	3898	367	11184	1066
24	2.05	113941	10840	3976	375	11407	1088
25	2.02	112273	10681	3918	369	11239	1072
26	2.04	113385	10787	3956	373	11351	1082
27	2.02	112273	10681	3918	369	11239	1072
28	2.01	111717	10629	3898	367	11184	1066
29	1.84	102269	9730	3568	336	10238	976
30	1.71	95043	9042	3316	312	9515	907
31	1.65	91708	8725	3200	302	9181	875
32	1.93	107271	10206	3743	353	10739	1024
33	1.90	105604	10047	3685	347	10572	1008
34	1.89	105048	9994	3666	345	10516	1003
35	1.78	98934	9412	3452	325	9904	944
36	2.02	112273	10681	3918	369	11239	1072
37	2.01	111717	10629	3898	367	11184	1066
38	1.79	99489	9465	3472	327	9960	950
39	2.04	113385	10787	3956	373	11351	1082
40	2.00	111162	10576	3878	366	11129	1061
41	2.01	111717	10629	3898	367	11184	1066
42	2.04	113385	10787	3956	373	11351	1082
43	1.95	108383	10311	3782	356	10850	1035
44	2.03	112829	10734	3937	371	11295	1077
45	2.09	116164	11051	4053	382	11629	1109
46	2.06	114497	10893	3995	376	11462	1093
47	2.04	113385	10787	3956	373	11351	1082
48	2.04	113385	10787	3956	373	11351	1082
49	1.98	110050	10470	3840	362	11017	1050
50	2.01	111717	10629	3898	367	11184	1066
51	1.98	110050	10470	3840	362	11017	1050
52	1.04	57804	5499	2017	190	5787	552

CHAPTER 8

INSTRUMENTATION AND METHODS OF ANALYSES

8.1 Introduction

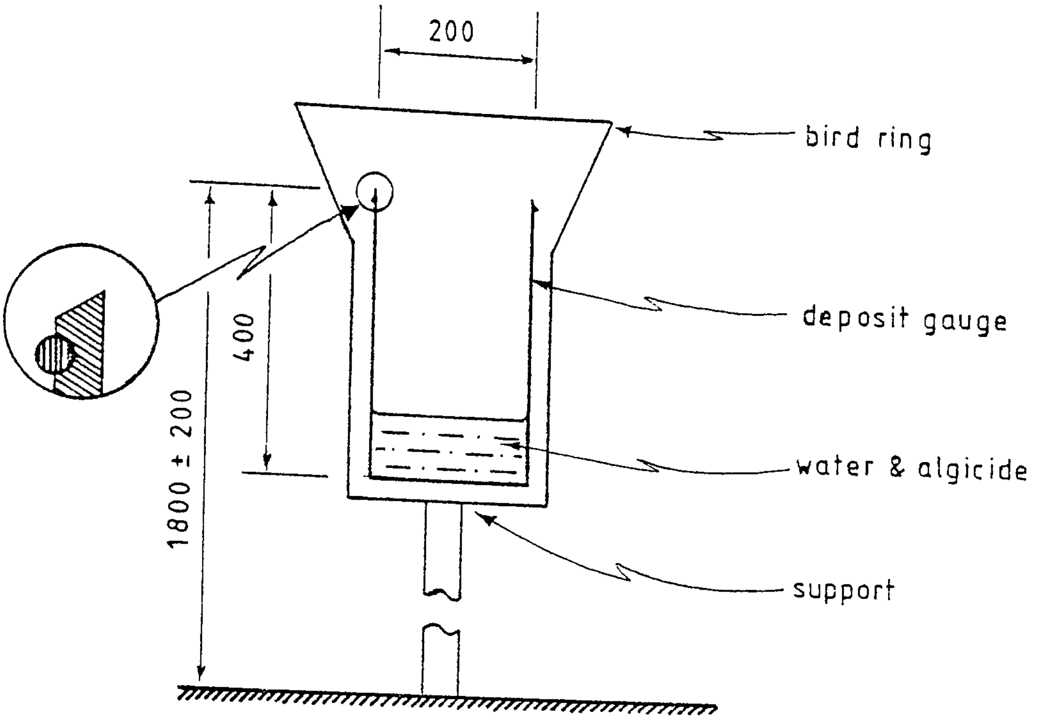
The sampling techniques and the methods of analyses used to collect the various data sets for this study will be discussed. All samples were analysed for the same seven heavy metals namely, iron, lead, zinc, copper, chromium, nickel and cadmium, using consistent techniques. The details of the analytical procedures are given fully in Appendix A and only a brief summary of these will be discussed here.

8.2 Atmospheric Deposition

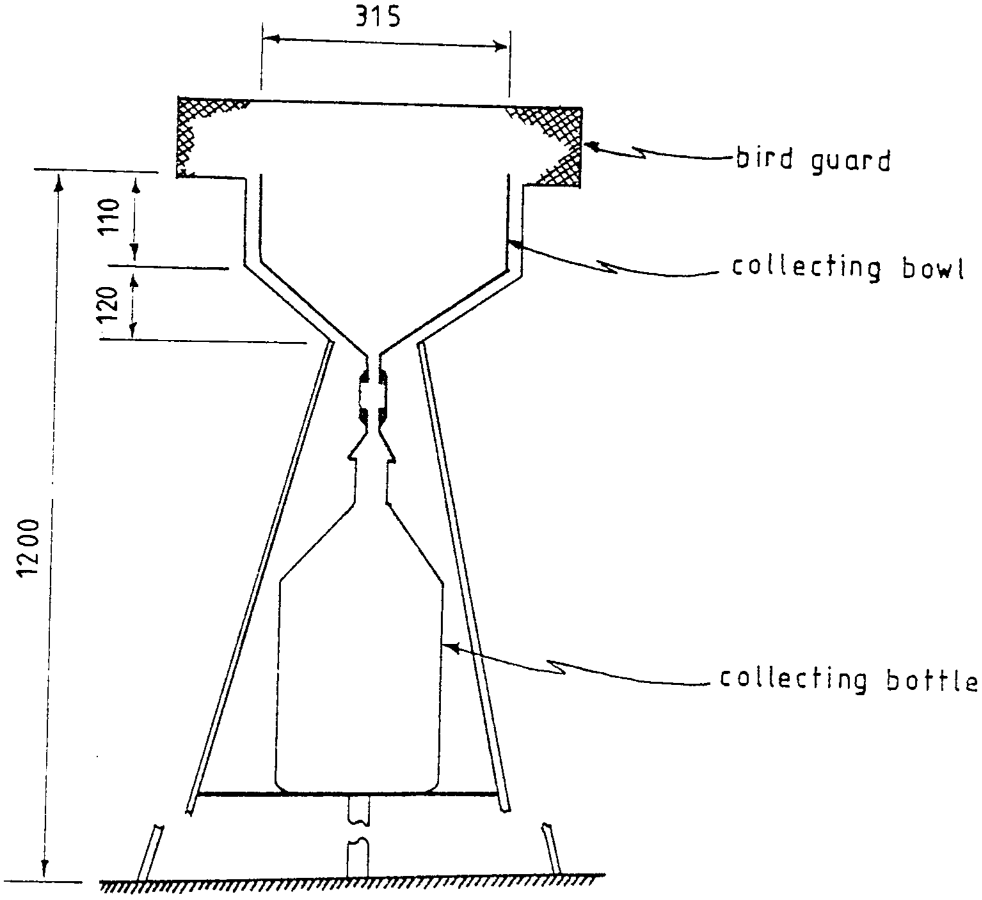
Atmospheric deposition was measured in this study by the deposit gauge method. Deposit gauges are designed to collect a representative sample of the deposition flux of particulate matter, and as such form the basis of all standardized measurement techniques. Horizontal deposit gauges collect vertically moving particles and will therefore give an estimate of the rate of metal input to the ground surface over a period of time. The physical collection of deposition flux is the best method for estimating gross metal input to a horizontal area. Deposit gauges offer the most accurate and precise method for quantifying the total metal inputs to an area (Simmons (1984)).

8.2.1 Measuring heavy metal deposition

There are two standard measurement instruments currently employed in deposition monitoring surveys in the UK. These are the Standard British Deposit Gauge (BS1747: Part 1), as shown in Figure 8.1 (b), and the International Standards Organization Gauge ((ISOG), shown in Figure 8.1 (a). Both standards necessitate the use of sampling instruments which are bulky, require elaborate support frames, have special siting requirements and are expensive to purchase and



(a) ISO deposit gauge



(b) BS 1747 :1 deposit gauge

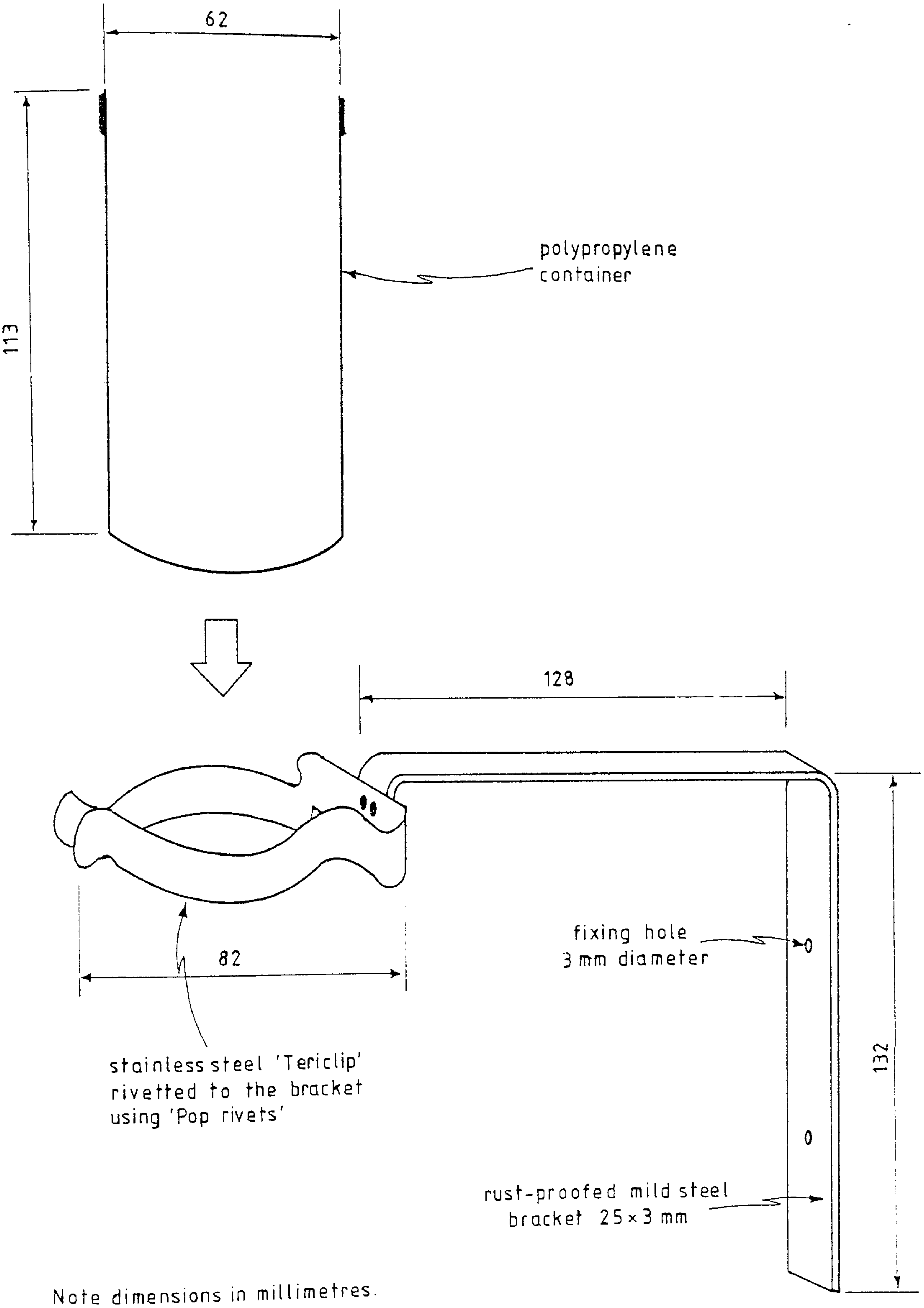
Figure 8.1 The ISO and British Standard deposit gauges.

maintain. These practical and technical difficulties have severely limited the number of sites that can be included in surveys of deposition in urban areas, as a result there has been a move towards simple alternative methods. However, the methods tend to be either qualitative (e.g. moss bags) or questions are raised regarding the technical validity of the siting strategy adopted for surveys in urban areas (e.g. jam jars on window ledges).

The new depostion measurement instrument used in this study, the deposit cannister, has been specifically designed for large scale surveys in urban areas and has been proven in the field by Simmons (1984).

The deposit cannisters were a simple plastic container approximately 60 mm in diameter and 120 mm in depth, see Figure 8.2 with sealing plastic 'clip-fit' lids, and were obtained from Johnsen and Jorgessen Plastics Limited, London. The cannisters were mounted on specially designed brackets (made from rust proof mild steel) with teri-clip attachments (made by Aston Services Limited, Birmingham), also shown in Figure 8.2, and were sited by attaching them to convenient supports.

In the Chelmsley Wood study, lampposts were used for the support where the deposit cannister was attached at a height of 5 to 6 m above ground level. Lampposts were chosen as suitable supports because they were ubiquitous in Chelmsley Wood and therefore a large number of cannisters could be sited at sufficient height within the catchment area. Solihull District Council kindly gave permission to use the lampposts.



Note dimensions in millimetres.

Figure 8.2 The deposit cannister and fixing bracket.

The deposit cannister is equivalent to a scaled down (1/3 size) International Standards Organization Gauge (ISOG), its use avoids many of the traditional difficulties associated with the monitoring of deposition in urban areas. The sampling instrument is cheap, light, versatile and easily constructed, and can be sited without the normal restrictions associated with current techniques. The siting height (typically 5 to 6 m as apposed to 1 to 2 m for the standard gauges) minimizes the problems of security and vandalism and reduces the possibility of contamination by locally resuspended dust. The measurement error of the deposit cannister has been found to be comparable to that of the standard deposit gauge methods (Simmons (1984)).

8.2.2 Siting Procedure

Using a simplified map, the catchment area was subdivided into a mesh comprising 20 equal units. The sampling framework was structured on this mesh covering the catchment and the deposit cannister locations were chosen at the nodes of the grid.

The deposit cannisters were washed thoroughly (see Appendix A), dried, sealed and stored in the laboratory until use. On site a suitable lamppost was identified as close to the predetermined sampling point as possible, taking into account the following site selection criteria:

(i) height of 5 to 6 m (± 1 m),
(ii) no immediate obstructions such as buildings, trees etc.,
(iii) easy access.

Through the use of an extension ladder the bracket was positioned and secured to the lamppost at the required height. The cannister was then unsealed, labelled and attached to the bracket. Practicle siting difficulties restricted the number of measurements that could be made at each lamppost, to a single cannister (a restriction placed on the survey by the Council for safety reasons).

Originally 24 deposit cannister sites were installed on this basis. However, in spite of being fixed 5 to 6 m above ground level on the lampposts, vandalism forced the network to be reduced to 11 rather random locations, (see Figure 8.3), which proved to be the least likely to be attacked during the course of the investigation. Nine cannisters per square kilometer were recommended by JURUE (1983) who developed this technique, and hence eleven would have given a representative sample for the whole catchment area, which was slightly over one square kilometer.

The cannisters were collected and replaced after 28 days and transported back to the laboratory for immediate analysis. The technical description of the analytical methods used to detect and quantify the total metals in the deposition samples is given in Appendix A. Briefly the method consisted of volume reduction by evaporation and wet ashing with aqua regia acid, followed by measurement by Atomic Absorption Spectrophotometry, abbreviated to AAS.

Since the deposit cannisters were left out for a period of 28 days the matter collected within would have been present on average for two weeks. Some particles may therefore have dissolved into the water, whilst others leached out.

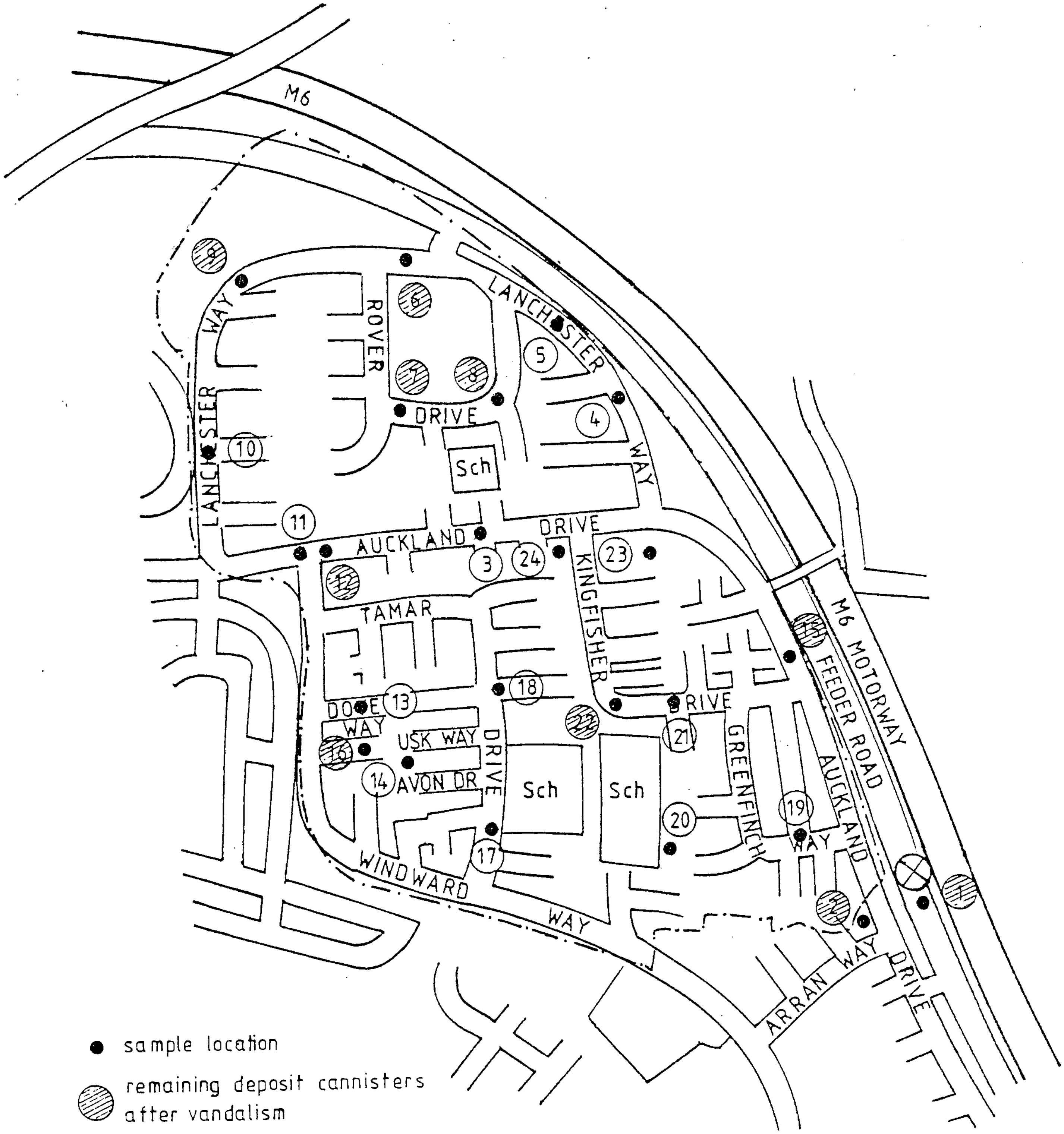


Figure 8.3 Deposit cannister and road sediment locations.

8.3 Road Surface Sediments

Roadside sediment samples were taken in order to acquire some indication of the heavy metal input to the stormwater drainage system from low level landborne sources. It should be noted, however, that the amount of sediment present, and hence its heavy metal content is only a measure of what was present at that particular locality and time. The material in the gutter will be very unevenly distributed due to the contour changes in the road surface and due to the redistribution by wind and water flow patterns. Material also accumulates in local depressions and hence samples from one part of the gutter will not be representative for the total length (Reinertsen (1981)). The majority of the road surface sediment samples were taken in the gutter next to the kerb. Even though the samples were not representative of the whole road, an indication would be given of the order of magnitude of the metal concentrations and loadings found on the road surface.

Road surface sediment samples were taken on the same sampling grid framework as for those of the deposit cannisters (see Figure 8.3). Initially samples were taken every 2 weeks for all 24 locations, but were gradually reduced to once per month at the deposit cannister locations.

Samples of roadside sediment (1 to 5 gm) were collected using small plastic scoops (80 x 40 mm), which had been washed and dried thoroughly between samples to prevent cross contamination. Each sample was then placed into a self sealing polythene bag (150 x 100 mm), labelled and taken to the laboratory for analysis. The samples were dried, ground and digested in aqua regia acid prior to analysis by AAS. For a detailed discussion see Appendix A.

8.4 Soil Samples

Samples of both topsoil and subsoil were taken at 10 random locations throughout the catchment, but where possible were located near to a deposit cannister/road surface sediment sampling site. The actual location of each was dependent upon local accessibility and therefore not all sites were consistent with those for the other data collection sites, see Figure 8.4.

A portion of topsoil, approximately 10 to 20 mm, was carefully removed from the surface of the soil using a stainless steel trowel, and was then placed in a labelled self sealing polythene bag (300 x 200 mm). Subsoil samples were taken from a depth of 20 to 150 mm using a plastic coated metal auger, which were also placed into a labelled polythene bag. Between each individual sampling event, both the trowel and auger were thoroughly cleaned to prevent cross contamination.

A number of samples were taken at each location and then bulked together to give a more representative sample. The samples were then returned to the laboratory for analysis using the same procedure as that for the road sediment samples (see Appendix A).

8.5 Stormwater Runoff

8.5.1 The Stormwater Recorder Station

The above ground apparatus were housed in a small wooden hut, located directly above a manhole on the 1.4 m diamter outfall sewer at a point where it left the catchment. The location was given in Figure 7.2. Flow data, stormwater samples and continuous water quality measurements were collected.

Figure 8.4 Soil sampling locations.

The discharge in the sewer was monitored continuously by an Arkon bubbler device which gave a continous trace of water levels on a paper chart. A stage-discharge relationship was supplied by Birmingham City Council. It was initially derived using suitable open channel flow formulae and subsequently supplemented and validated by current meter and volumetric rating. The stage-discharge relationship was mounted on a microcomputer to facilitate the conversion of Arkon levels to actual discharge values.

A peristaltic pump (Watson and Marlow HRSP) was employed to raise the stormwater from the sewer into the equipment hut at a rate of 450 l/hour. The sampling cycle was triggered when the water level in the sewer rose above the initiation probe level and made contact with the two poles of the sensor. Sampling commenced when the flow was appproximately three times the normal dry weather flow (90 l/sec). On entering the hut, the flow was divided, half passed to the sampler and half flowed through the Phox water quality monitoring system.

Stormwater samples were collected by an automatic Rock and Taylor multipurpose liquid sampling machine, housed in the recorder station. It had been designed to take up to 48 discrete samples at preset time intervals (3 minutes). When the sampling cycle was initiated by the rising water level in the sewer, a timing device (ACU Sedeco timer) printed out the initiation time and the corresponding time for each sample taken. The samples were distributed by a rotary arm into 500 ml polythene bottles. After each sample was taken, the pipes were back flushed to prevent contamination of the next sample, any excess flow from the sample was diverted to an overflow pipe and returned to the sewer.

As the storm passed, the level of water in the sewer subsided and fell below the initiating sensor probe which terminated the sampling cycle.

Immediately after each storm the full bottles were collected and taken to the laboratory for analysis, and replaced with a clean set of bottles. The analysis involved separating the particulate and soluble matter by filtration through 0.45 micron membrane filters. Both the particulate and soluble matter were then analysed by AAS. Details of the analytical procedure used are presented in Appendix A.

8.5.2 The Phox System

Phox Systems Limited designed a multi parameter water quality system, which recorded turbidity, dissolved oxygen, conductivity, chloride, pH and temperature, continuously throughout a storm runoff event at predetermined intervals.

The Phox system was installed after commencement of the sampling period and some teething problems were experienced, as a result not all storms were monitored.

The Phox system consisted of a series of cells, some containing probes where the parameters were monitored, see Plate 8.1. The cells which contained the pH and chloride probes were specially designed for the instrument. The measured levels were recorded on a 6 channel paper chart (see Plate 8.2).

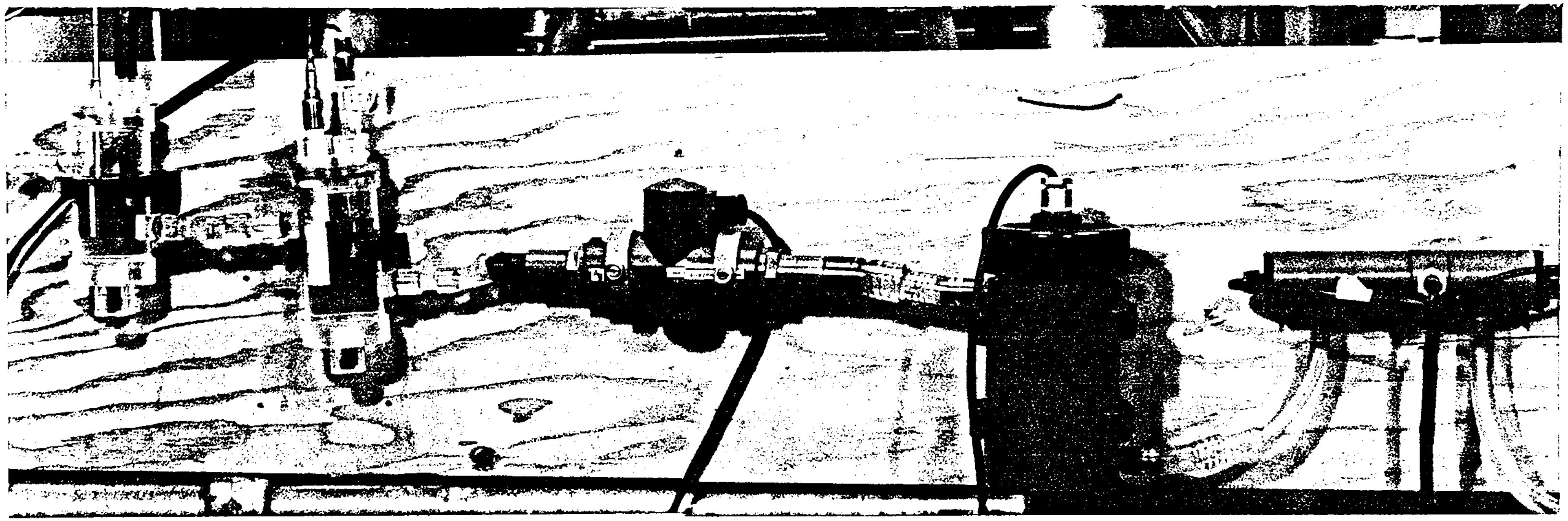


Plate 8.1 Layout of Phox monitoring cells.

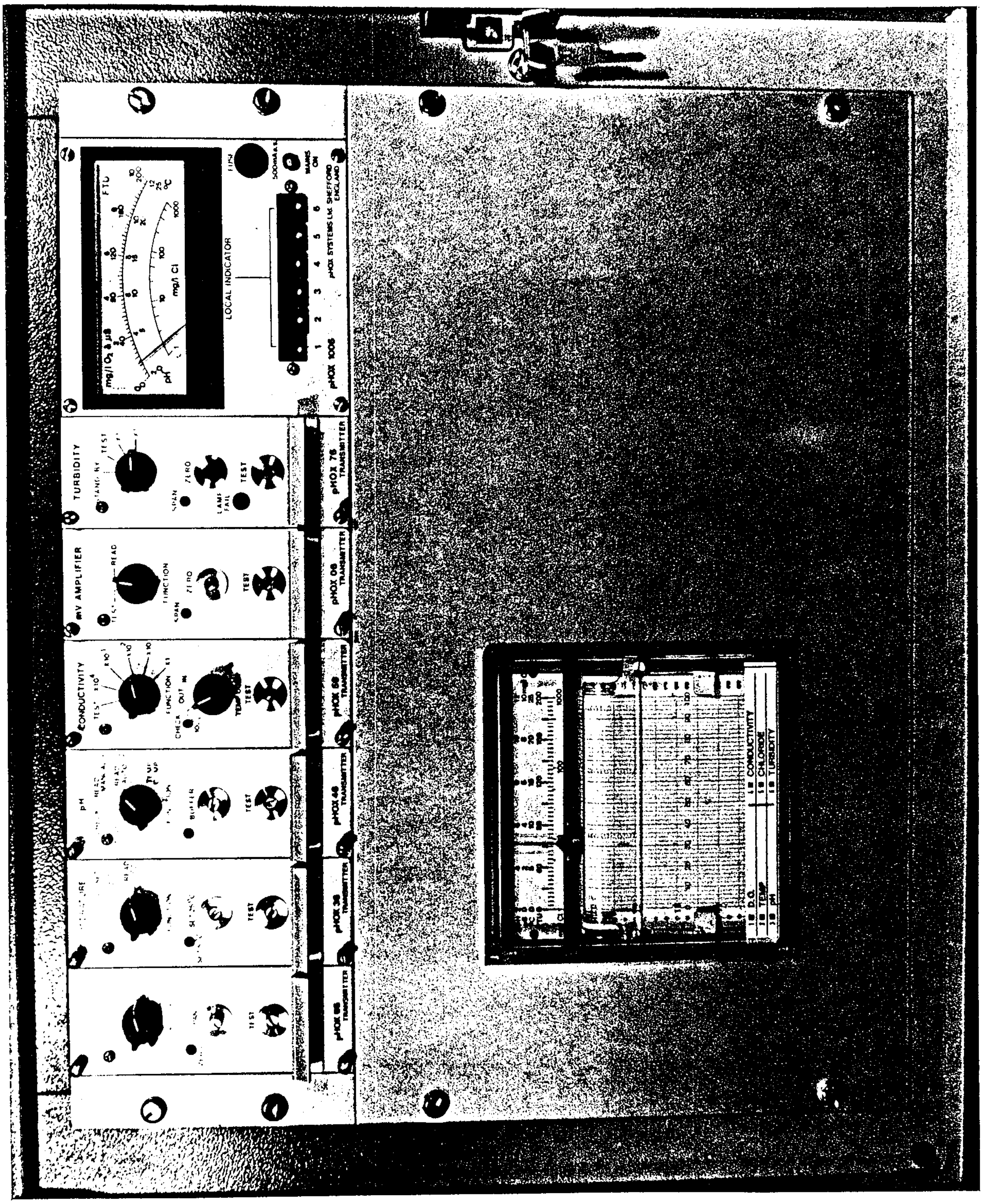


Plate 8.2 The Phox monitoring device.

The sequence in which the flow passed through the various cells was important, as some probes were known to affect the other probes (e.g. pH probe would affect the chloride probe). The sequence of probes for least interference was chosen to be, turbidity, oxygen, conductivity, chloride, and finally pH and temperature. After passing through the system the flow was returned to the sewer.

Prior to installation in the field, the Phox system was tested and calibrated in the laboratory using fresh stormwater samples. Each parameter measured on the instrument was validated by the results obtained by standard analytical techniques, all of which were found to be consistent. Once in the field, the instrument was cleaned and recalibrated either after each storm event or once a week when few storms occurred.

Amongst the many teething problems encountered following installation were leakages, obtaining a sufficient flowrate past the various probes (a more powerful pump had to be purchased) and the installation of a flushing device to clean the cells and probes after each event and to keep them in a sterile environment.

The reasons for installing the Phox system alongside the automatic sampler was for the acquisition of additional water quality data and to check whether samples taken by the discrete sampler were in fact representative of the flow at the time of sample. The discrete samples essentially provide an average of pollutant concentrations over the sampling period. If the samples were taken during a peak or trough in pollutant concentration it is possible for an over or under estimation of the actual levels to result.

8.6 Data Management

The wide ranging nature of the study resulted in the acquisition of a large volume of data. In order to handle the data a data base management system (dBASE II), on various microcomputers (Osborne and Apricot), was employed. This allowed filed records to be stored and searches to be performed for data meeting specific criteria. The required information could then be output in a form that could be immediately manipulated by other packages (e.g. Supercalc 3 and Abstat) and Basic programs on the same machines. The raw data obtained from the analysis of the deposit cannister, road sediment, soil and stormwater samples are given in Appendix C.

8.7 Statistical Theory and Application to the Study

8.7.1 Regression Analysis

Regression analysis is a technique frequently used to determine a relationship between two or more variables that are causally related, in this case, the individual heavy metal concentrations. In the simple two factor case the dependent variable (y) can be linearly related to the independent variable (x), by the regression function:

$$y^1 = a + b\,x \tag{8.1}$$

where: $a = \bar{y} + b\,\bar{x}$

and $$b = \frac{\sum x\,y - \frac{\sum x \sum y}{n}}{\sum x^2 - \frac{(\sum x)^2}{n}}$$

The regression coefficients a and b are selected in such a way that the sum of the squared residuals $(y - y^1)^2$ are minimized. This is the Least Squares criterion which implies that any other value of a and b would yield a larger value of $(y - y^1)^2$. The correlation between the independent variable and the residual values $(y - y^1)^2$ is reduced to zero.

8.7.2 The Correlation Coefficient

This is a measure of the closeness of fit of a regression line to the distribution of observations. The closer the correlation coefficient is to 1 or - 1 then the greater the amount of variance has been explained (or removed) by the regression line.

The correlation coefficient was used in the study to give an indication of any relationship that existed between the individual metals and various other parameters. Correlation matrices were computed to illustrate the relationships between paired parameters.

CHAPTER 9

HEAVY METAL DEPOSITION

9.1 Introduction

Having previously described the experimental catchment in Chapter 7, the heavy metal deposition associated with the area will now be discussed in detail.

Currently there is no centrally co-ordinated network for monitoring metal deposition in the UK equivalent to the national survey of smoke, SO_2 and airborne metals (McInnes (1979)). Some individual local authorities carry out routine deposition monitoring but there is no standardization of methods or siting policy and as a result much of the information obtained is of limited value (DOE (1974)).

Deposition rates for iron, lead, zinc, copper, chromium, nickel and cadmium measured at various urban, rural and remote locations are summarized in Table 9.1 (adapted from Simmons (1984)). The studies reported here are confined to those where standard 'deposit gauge' measurements have been used, in order to compare the results with those obtained in this study. Deposition rates for lead show a range of six orders of magnitude, from 0.0001 $mg/m^2/30$ days in the remote antartic, to greater than 100 $mg/m^2/30$ days near large industrial areas and the deposition rates for cadmium show a range of five orders of magnitude. Table 9.1 also indicates that there are large differences between remote, rural and urban areas, and even in urban areas deposition levels more typical of rural areas are sometimes observed.

9.2 Heavy Metal Deposition within the Study Area

As previously detailed in Section 8.2 the deposit cannisters remained active on site for a period of 28 days, the contents were then analysed to determine the heavy metal deposition rate. In order to calculate the average total deposition for each metal over the catchment area, during each sampling period, two methods were employed namely, the arithmetic mean method and the Thiessen polygon approach. The latter of which is commonly used to calculate average areal precipitation.

9.2.1 Arithmetic Mean Method

The simplest method was to calculate the arithmetic mean of the metal deposition rates for each sampling period. This entailed the summation of values obtained for all of the deposit cannisters, irrespective of their position, and then obtaining the average. The values obtained were then divided by the surface area of the cannister in order to obtain deposition rates in mg/m^2/28 days. These results are shown in Table 9.2.

Providing there is an even distribution of cannisters within the study area, the technique will give satisfactory results. However, the deposit cannister sites were unevenly distributed (due to the reduction in numbers forced by vandalism), as a result the average may be biased and not representative of the whole catchment area, therefore another technique based on the Thiessen polygon method, normally used for raingauge measurements, was employed.

METAL	REMOTE		RURAL		URBAN	
Fe	-		10 - 20	9,12	15 - 150	5,6,8
Pb	1E-4 - 6.5E-3	2,10	0.18 - 1.7	3,14	1.2 - 8.3	8,11
Zn	1E-4	2	0.10 - 15	4,12,13, 16	5.0 - 50	1,5,6, 11,12
Cu	1E-4 - 1E-3	2,4	0.08 - 4.0	1,4,9,10, 12,13	0.1 - 65	5,6,11 12
Cr	-		0.2 - 4.0	4,12,13	0.2 - 2.0	5,12
Ni	-		0.07 - 12.1	4,12,13	0.1 - 4.1	6
Cd	3.1E-4 - 1.9E-4	10,2	0.01 - 0.21	13,16	0.05 - 0.11	6,14

Table 9.1 Typical levels of iron, lead, zinc, copper, chromium, nickel and cadmium deposition ($mg/m^2/30$ days). (adapted from Simmons (1984))

3.1E-4 = 3.1×10^{-4}

1	Anderson et al (1978)	9	Hallett et al (1982)
2	Boutron (1979)	10	Herron et al (1977)
3	Cawse (1974)	11	Lazarus et al (1970)
4	Cawse (1977)	12	Pattenden (1974)
5	Cawse and Turner (1981)	13	Pierson et al (1973)
6	Duggan and Burton (1983)	14	Rohbock et al (1981)
7	Galloway et al (1980)	15	Schlesinger et al (1974)
8	Georgii et al (1984)	16	Struempler (1976)

9.2.2 Thiessen Polygon Approach

The use of Thiessen Polygons (Thiessen (1911)) makes some allowance for the uneven distribution of cannisters throughout the area, and also allows data from adjacent areas, where available, to be incorporated into the calculations. In this approach, which is illustrated in Figure 9.1, perpendicular bisectors were drawn through the straight lines joining adjacent gauges, leaving each gauge in the centre of the polygon, which varied in size according to the spacing of the cannisters. The area covered by each polygon, or part of a polygon was calculated and this weighted area factor then applied to the appropriate cannister metal deposition total. The reduced totals were then summed to give the average total metal deposition for the whole catchment taking into account the surface area of the deposit cannister, the figures are presented in Table 9.3.

Since the number and hence spacing of the gauges varied for each sampling period new sets of polygons had to be drawn for each sampling period, a sample of which is shown in Figure 9.2.

On comparison of Table 9.2 with Table 9.3 it can be observed that the calculated average metal deposition rates from both methods were very similar. However, results obtained using the Thiessen Polygon approach will be used in the study to account for the uneven distribution and variable number of cannisters employed.

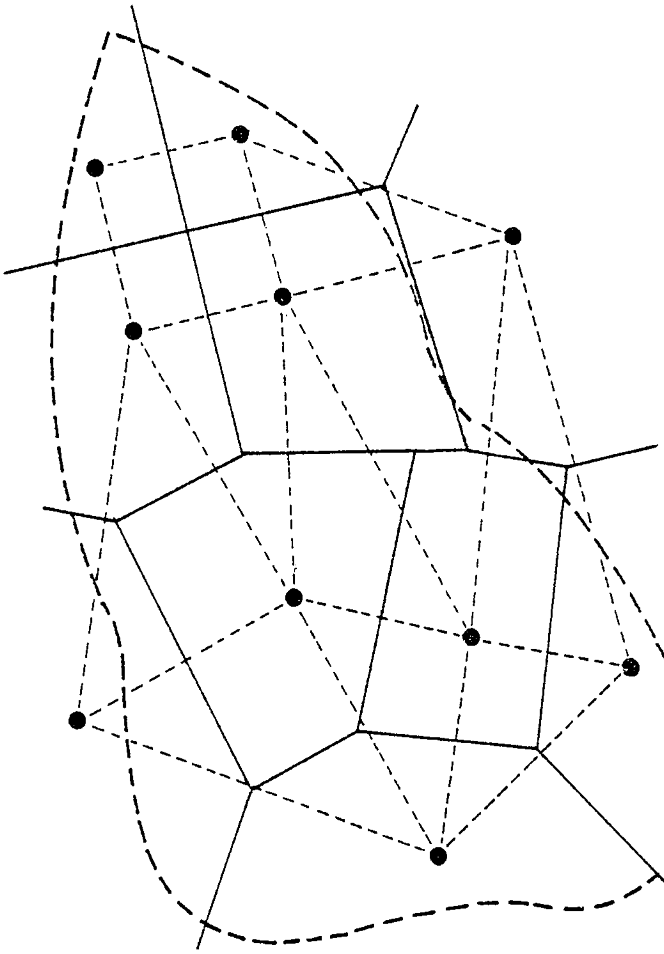


Figure 9.1 Thiessen polygon method for the determination of average precipitation over a catchment area.

Figure 9.2 Thiessen polygons drawn for the Chelmsley Wood catchment for the date 17/8/83.

DATE	IRON	LEAD	ZINC	COPPER	CHROMIUM	NICKEL	CADMIUM	TOTAL
17/08/83	54.07	2.48	3.88	1.33	-	0.268	0.074	62.10
14/09/83	40.78	3.33	4.35	1.35	-	-	0.102	49.92
12/10/83	29.81	3.40	3.26	0.70	-	-	0.035	37.22
09/11/83	18.11	2.95	3.62	0.73	0.26	0.354	0.025	26.05
07/12/83	18.16	2.55	2.72	0.68	0.03	0.527	0.127	24.81
04/01/84	16.53	2.25	1.69	0.45	0.14	0.329	0.124	21.52
01/02/84	19.27	2.89	3.68	0.74	0.16	0.622	0.060	27.44
29/02/84	35.39	4.02	4.95	1.11	0.25	0.286	0.071	46.09
28/03/84	41.04	4.64	4.52	1.07	0.21	0.088	0.049	51.62
25/04/84	29.99	2.41	3.27	0.76	0.31	0.339	0.148	37.23
23/05/84	50.83	3.66	2.74	0.73	0.27	0.354	0.446	59.04
20/06/84	57.98	3.93	2.16	0.97	0.15	0.626	0.085	65.90
18/07/84	36.62	2.48	2.67	0.87	0.30	0.771	0.124	43.88
Mean	35.51	3.15	3.35	0.88	0.16	0.351	0.113	42.52
Std. dv.	14.20	0.75	0.95	0.27	0.12	0.239	0.107	14.90

Table 9.2 Average heavy metal deposition using the Arithmetic Mean Method for Chelmsley Wood. (mg/m^2/28 days)

DATE	IRON	LEAD	ZINC	COPPER	CHROMIUM	NICKEL	CADMIUM	TOTAL
17/08/83	54.44	2.11	3.73	1.39	-	0.14	0.065	61.88
14/09/83	43.35	3.24	4.45	1.41	-	-	0.08	52.52
12/10/83	33.68	2.72	3.84	0.92	-	-	0.03	41.20
09/11/83	17.12	2.49	3.53	0.70	0.29	0.24	0.03	24.41
07/12/83	19.40	2.41	2.89	0.78	0.05	0.57	0.15	26.26
04/01/84	17.66	2.35	1.73	0.45	0.19	0.38	0.10	22.86
01/02/84	20.79	2.88	3.74	0.78	0.20	0.78	0.08	29.26
29/02/84	37.15	3.60	4.97	1.07	0.24	0.26	0.07	47.37
28/03/84	44.28	3.82	4.60	1.07	0.17	0.04	0.04	54.03
25/04/84	30.85	2.15	3.30	0.76	0.25	0.23	0.13	37.68
23/05/84	59.25	3.27	2.81	0.77	0.26	0.24	0.42	67.03
20/06/84	63.54	3.43	2.21	0.92	0.16	0.63	0.15	71.05
18/07/84	36.65	2.14	2.66	0.88	0.27	0.69	0.13	39.43
Mean	36.78	2.82	3.42	0.91	0.16	0.32	0.16	44.23
Std. dv.	15.78	0.60	0.95	0.27	0.11	0.27	0.18	16.32

Table 9.3 Average heavy metal deposition using Thiessen Polygon Approach for Chelmsley Wood (mg/m^2/28 days).

9.3 Comparison with Contemporary Studies

Table 9.4 is a summary of the mean values and ranges for the metal deposition rates observed in the study. When compared with values obtained from contemporary studies, which are shown in Table 9.5 (adapted from Simmons (1984) with figures adjusted for the units mg/m^2/28 days), it can be seen that the metal deposition rates obtained for Chelmsley Wood were compatible to those from other related studies. Since the Chelmsley Wood area was urban/residential, levels would not be expected to reach those normally associated with solely urban areas. In some cases the metal deposition rate at the site was very low and indicative of a rural area (e.g. zinc, copper, chromium and nickel), whereas other metal deposition rates were comparative to an urban environment (e.g. iron and lead). One dubious result was obtained for cadmium (0.42 mg/m^2/28 days), however, this was most likely due to contamination and was therefore disregarded. Once this adjustment had been made the results for cadmium fell within the limits expected of a rural area.

The ranges of metal deposition were also seen not to display significant variation when compared with the large spatial variability of metal deposition near industrial sources of metal pollution. It can therefore be concluded that this area of Chelmsley Wood was not subject to significant levels of heavy metal deposition when compared with those for industrial areas. The average metal deposition rates found in Chelmsley Wood during the study period were within the rates reported for other rural/urban areas.

Metal	Mean	Standard deviation	Range
Iron	36.78	15.77	17.12 - 59.25
Lead	2.82	0.60	2.11 - 3.82
Zinc	3.42	0.95	1.73 - 4.97
Copper	0.91	0.27	0.45 - 1.41
Chromium	0.16	0.11	0.0 - 0.29
Nickel	0.32	0.27	0.0 - 0.78
Cadmium	0.16	0.18	0.03 - 0.15 (0.42)
Total	44.23	16.32	22.86 - 71.05

Table 9.4 Mean and range of mean heavy metal deposition in Chelsley Wood (mg/m^2/28 days).

Metal	Rural range	Urban range
Iron	9.0 - 19.0	14.0 - 140.0
Lead	0.075 - 1.59	1.12 - 7.75
Zinc	0.093 - 14.0	4.66 - 46.66
Copper	0.075 - 3.73	0.093 - 60.67
Chromium	0.186 - 3.73	0.186 - 1.86
Nickel	< 0.065 - 11.29	0.093 - 3.83
Cadmium	0.0093 - 0.196	0.0186 - 0.103

Table 9.5 Ranges for heavy metal deposition from contemporary studies (mg/m^2/28 days). (adapted from Simmons (1984))

9.4 Correlation between Metal Deposition

Correlation matrices were calculated on a microcomputer to investigate any significant relationship between the various metals within the deposit cannister samples. Correlation matrices were computed for all the deposit cannister results bulked together (Table 9.6) and for each month individually.

The correlation matrix for the full deposit cannister data set displayed no significant correlation between any two metals and the highest correlation coefficient observed was 0.6 between copper and zinc.

It was apparent after consideration of the correlation matrices for each month, that different patterns tended to emerge throughout the year.

During the months of November and December reasonable correlations were found to exist between (the correlation coefficients are given in the parentheses i.e. 'r'):

Fe : Cu (0.89)   Fe : Cr (0.90)   Fe : Ni (0.86)
Cr : Cu (0.84)   Ni : Cu (0.92)   Ni : Cr (0.86)

The month of January displayed more significant correlations, namely:

Fe : Pb (0.80)   Fe : Zn (0.85)   Fe : Cu (0.85)
Fe : Cr (0.90)   Zn : Pb (0.83)   Cr : Cu (0.84)
Cu : Pb (0.80)

Despite the overall random appearance of any relationship, the comparatively strong correlations displayed in the month of January would appear to suggest a common dominant source of metal contamination. This could have been as a result of de-icing road salt resuspended in the atmosphere due to the spray from vehicles. Salting within the area was initiated in November and was particularly heavy during January. A similar pattern of de-icing activity would have been in operation from the adjacent M6 motorway and the aerosols produced could have been carried over the catchment by prevailing winds.

At other times during the year reasonable correlations were observed but no relationship could be identified. Good correlations were observed particularly during the months of September to October for copper and zinc (0.82) and similarly in April (0.89). June and July also displayed significant correlations between chromium and iron (0.91). During the other months of the year no significant correlations were observed.

Table 9.7 summarizes the correlations observed at various times throughout the sampling period. It would appear that the possibility of using an individual metal to infer the concentration of any other, at any time throughout the sample period, is slight due to the lack of observation of any consistent monthly correlations, of any significance, between the various metals within the deposit cannister samples. It is therefore necessary to look at each metal on an individual basis.

METAL	Iron	Lead	Zinc	Copper	Chromium	Nickel	Cadmium
Iron	1.0						
Lead	0.29	1.0					
Zinc	0.35	0.43	1.0				
Copper	0.45	0.34	0.60	1.0			
Chromium	0.17	0.22	0.14	0.07	1.0		
Nickel	0.06	0.16	0.03	0.12	0.24	1.0	
Cadmium	0.11	0.045	0.015	-0.012	0.17	0.14	1.0

Table 9.6 Correlation Matrix for the entire deposit cannister data set.

Metal correlation	Correlation coefficient
Fe : Pb	0.80
Fe : Zn	0.85
Fe : Cu	0.85, 0.89
Fe : Cr	0.90, 0.89, 0.91
Zn : Pb	0.83
Cu : Zn	0.89, 0.82
Cr : Cu	0.80, 0.84
Ni : Cu	0.92
Ni : Cr	0.86

Table 9.7 Correlation coefficients for the deposit cannister samples.

9.5 Metal Proportions

For each of the seven metals determined, the ratio of each metal to the total metal content was calculated, expressed as a percentage, and the results are presented in Table 9.8 and Figure 9.3. The main objective of this particular analysis was to enable comparisons to be made between the various data sets, since each were measured in different units and as a result any direct comparison of actual concentrations was not possible (see Chapter 13).

It was clear that iron predominated within all of the samples throughout the year, and ranged from approximately 66 to 85.5% with a mean percentage of 78%. Lower percentages of iron were seen to occur during the winter (i.e. from November to February) which may have been due to the winter salting period when the percentage of other metals increased, forcing iron percentages to decrease. Alternatively the higher percentages of iron in the summer may have been due to drier weather conditions and more intense agricultural activity creating more resuspended dust.

Because the iron proportions were so high within all samples, and tended to mask the changes that occurred for other metals, the calculations were repeated with the exclusion of iron. The non-ferrous metal proportions obtained, again expressed as a percentage, are presented in Table 9.9 and in Figure 9.4.

Zinc and lead proportions were now shown to predominate and had mean percentages of 42 and 38% respectively. The proportions of zinc were slightly higher than those of lead and ranged from 30 to 49%. The quantities for both metals remained reasonably consistent throughout the year.

DATE	PERCENTAGES						
	IRON	LEAD	ZINC	COPPER	CHROMIUM	NICKEL	CADMIUM
17/08/83	85.55	4.58	6.82	2.42	-	0.48	0.13
14/09/83	80.93	6.84	9.24	2.74	-	-	0.23
12/10/83	79.10	10.23	8.66	1.85	-	-	0.14
09/11/83	66.94	12.03	15.20	3.07	1.01	1.54	0.12
07/12/83	72.32	10.71	11.31	2.73	0.15	2.27	0.47
04/01/84	76.14	10.59	8.19	2.21	0.69	1.47	0.67
01/02/84	65.72	12.50	15.16	3.02	0.58	2.64	0.35
29/02/84	75.96	8.33	11.64	2.56	0.64	0.65	0.18
28/03/84	79.32	8.97	8.84	2.10	0.42	0.22	0.09
25/04/84	79.86	6.62	9.24	2.10	0.82	0.94	0.40
23/05/84	84.50	7.11	4.99	1.27	0.53	0.69	0.87
20/06/84	82.40	8.36	5.02	2.32	0.31	1.38	0.16
18/07/84	82.42	6.05	6.56	2.09	0.66	1.85	0.38
Mean	77.78	8.69	9.30	2.34	0.45	1.16	0.32
Std.dev.	5.98	2.33	3.17	0.47	0.32	0.73	0.23

Table 9.8 Deposit Cannister ferrous metal proportions.

DATE	PERCENTAGES					
	LEAD	ZINC	COPPER	CHROMIUM	NICKEL	CADMIUM
17/08/83	29.59	48.88	17.91	-	2.76	0.82
14/09/83	35.75	48.27	14.78	-	-	1.18
12/10/83	47.57	41.98	9.76	-	-	0.67
09/11/83	36.34	46.07	9.65	3.63	3.94	0.34
07/12/83	38.04	41.66	10.06	0.49	7.92	1.80
04/01/84	43.62	34.79	9.44	3.23	6.04	2.85
01/02/84	35.91	45.28	9.09	1.95	7.07	0.68
29/02/84	33.84	49.16	10.84	2.50	2.85	0.78
28/03/84	41.63	44.50	10.23	1.96	0.99	0.47
25/04/84	32.31	46.29	10.65	4.21	4.47	2.04
23/05/84	43.92	33.98	8.86	3.39	4.05	5.76
20/06/84	46.36	30.37	11.94	2.05	7.99	1.25
18/07/84	34.28	37.63	12.21	3.97	10.15	1.72
Mean	38.40	42.22	11.19	2.11	4.48	1.57
Std.dev.	5.45	5.95	2.47	1.50	3.09	1.39

Table 9.9 Deposit Cannister non-ferrous metal proportions.

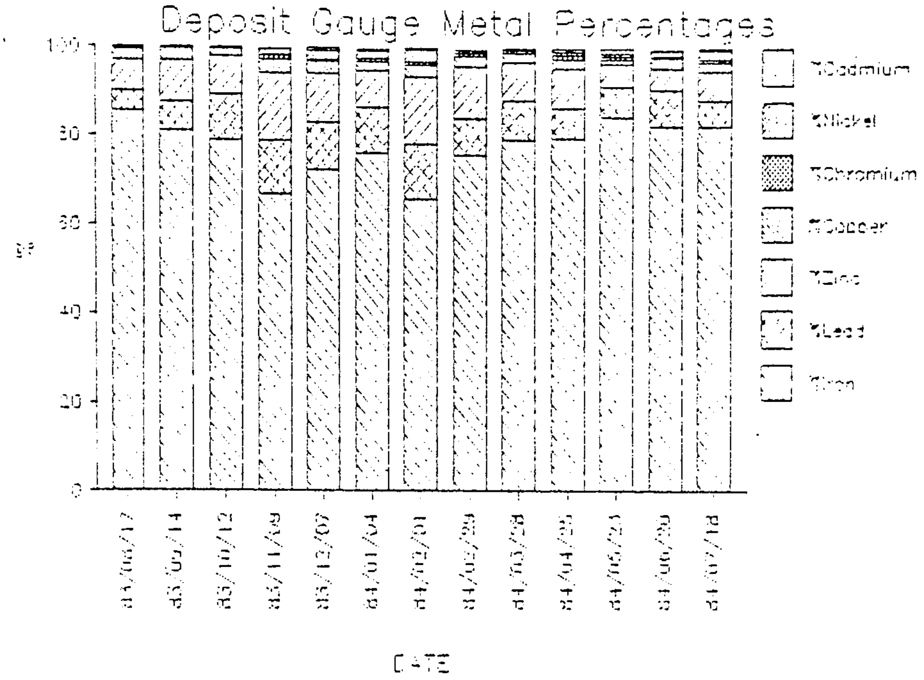


Figure 9.3 Deposit gauge metal percentages including iron.

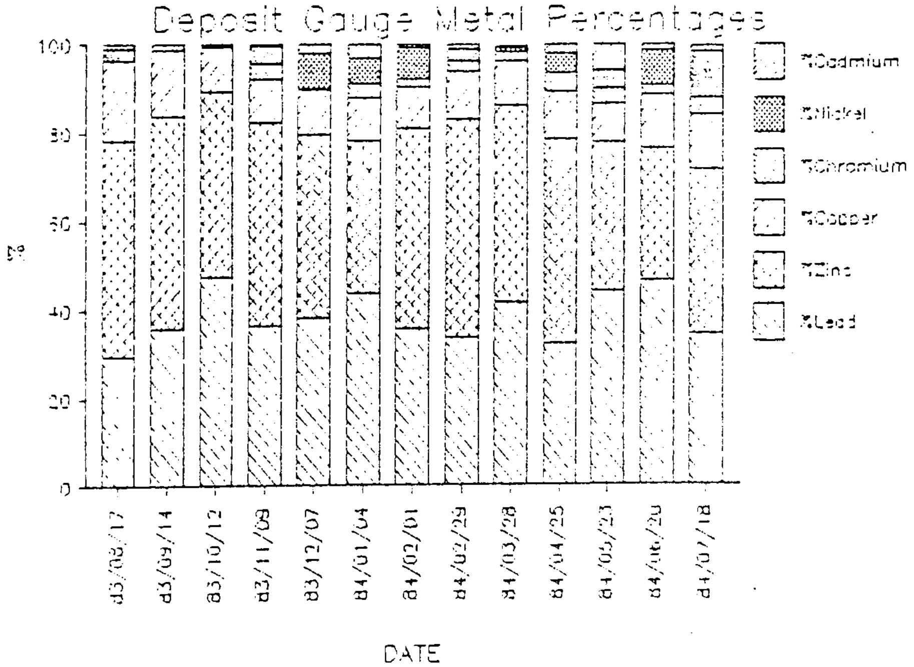


Figure 9.4 Deposit gauge metal percentages excluding iron.

9.6 Temporal Variation in Metal Deposition

Pronounced seasonal variation in airborne concentrations of metals such as lead and cadmium have been observed at many locations. In Great Britain winter maxima have commonly been found (Solomon et al (1978)) and have been attributed to a combination of an increased use of fossil fuels and a change in meterological factors governing the dispersion of airborne pollution. For deposition, however, no clear relationship between deposition rate and the season of the year has been established. Hedley and Lockley (1975) observed that dust deposition exhibited no pronounced seasonal trend and did not appear to follow the patterns for runoff quality. However, in a study by Rossano and Johnson (1966) seasonal variations in dustfall were observed, with maximum values occurring in March, April and May, during the rest of the year the levels remained relatively constant.

Deposition is strongly influenced by discharges from localized sources which often tend to be random and sporadic in nature. Pattenden and Branson (1982) for example, found no clear seasonal trend in the deposition of lead and cadmium in the vicinity of a copper refinery in Walsall and attributed the variations observed to localized sources of emission.

9.6.1 Temporal Variation in Metal Depostion in Chelmsley Wood

Meteorological data for wind (duration, speed and maximum gust), total daily sunshine hours, rainfall, relative humidity and temperature were obtained throughout the study period. In order to correlate the meteorological parameters to those of measured deposition rates, the average meteorological conditions for each sampling period were calculated and are presented in Figure 9.5.

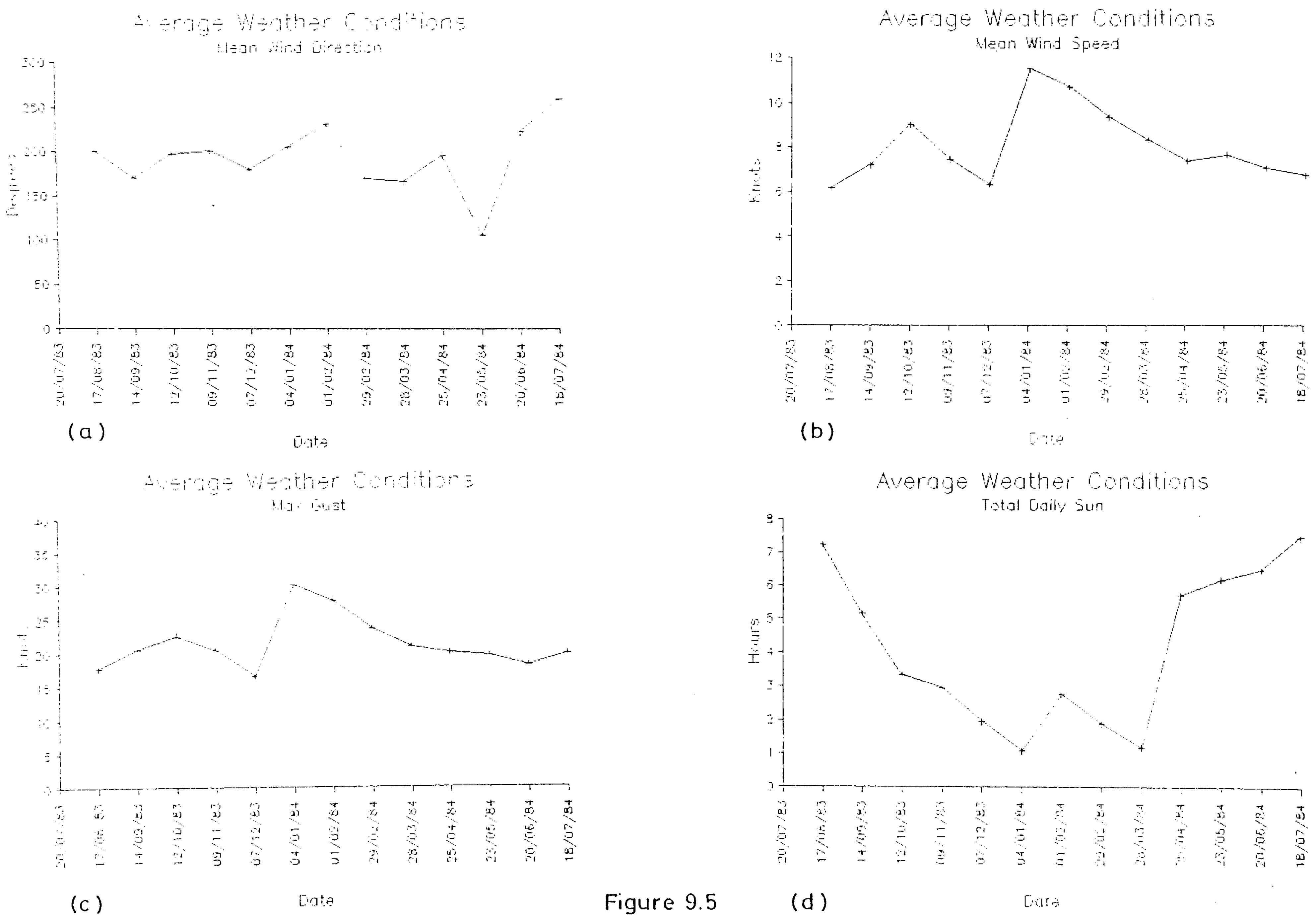
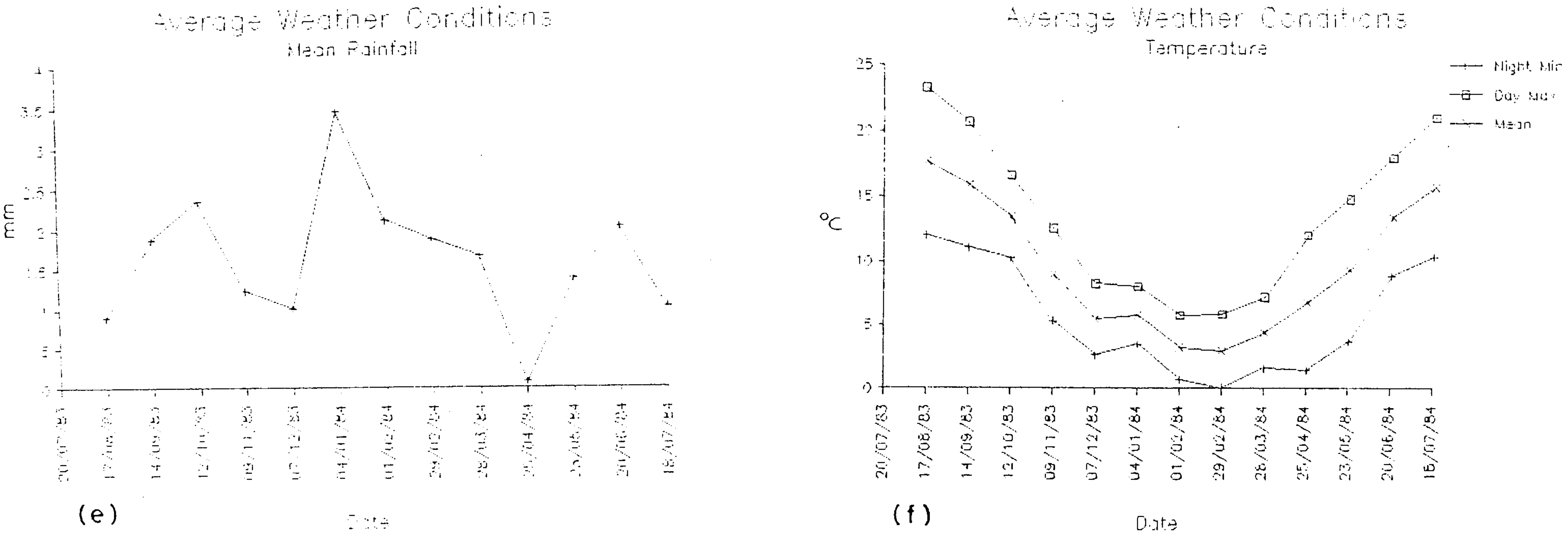

Average Weather Conditions
Mean Wind Direction
Degrees
0
50
100
150
200
250
300
20/07/83
17/08/83
14/09/83
12/10/83
09/11/83
07/12/83
04/01/84
01/02/84
29/02/84
28/03/84
25/04/84
23/05/84
20/06/84
18/07/84
Date
(a)
Average Weather Conditions
Mean Wind Speed
Knots
0
2
4
6
8
10
12
Date
(b)
Average Weather Conditions
Max Gust
Knots
0
5
10
15
20
25
30
35
40
Date
(c)
Average Weather Conditions
Total Daily Sun
Hours
0
1
2
3
4
5
6
7
8
Date
(d)

Figure 9.5



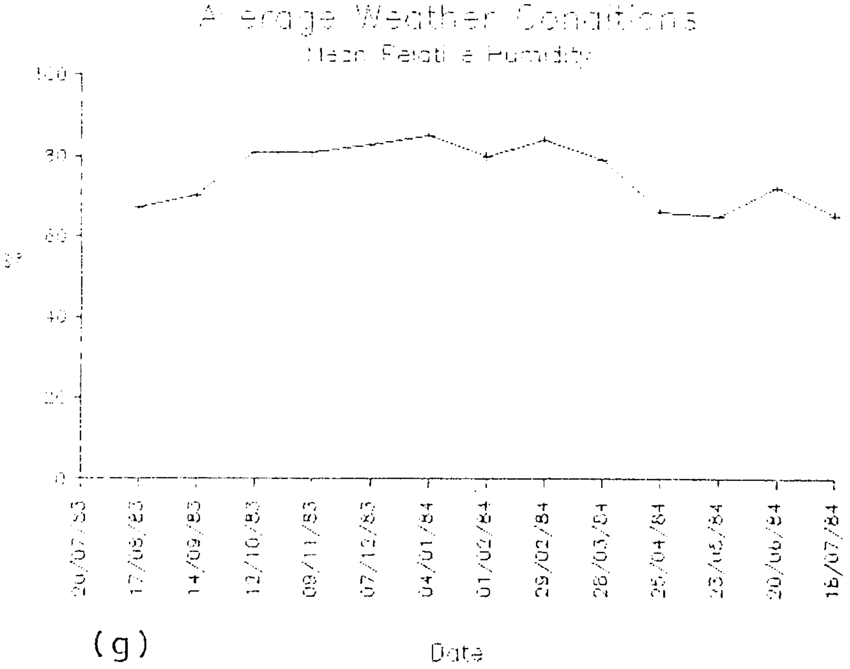


Figure 9.5 cont.

Wind directions are known to have an affect on deposition within certain areas (Simmons (1984)), therefore wind roses were drawn for each sampling period, an example of which is given in Figure 9.6. A study of the wind roses indicated that the number of wind days from a given sector had a substantial influence on the deposition rate. The number of wind days in a given sector was therefore calculated and are shown in Table 9.10.

9.6.1.1 Total Metals

A distinct seasonal pattern in total heavy metal deposition over the catchment can be seen in Figure 9.7 (a). Highest levels occurred during the summer months of June to August with a peak of approximately 70 mg/m^2/28 days in June. Deposition levels fell during the winter months (i.e. from November to February), achieving a minimum of approximately 20 mg/m^2/28 days in January. The variations may be purely due to the seasonal meteorological conditions since close agreement can be observed when Figure 9.7 (a) is compared with similar plots for the average meteorological conditions during each sampling period, as shown in Figure 9.5. The meteorological conditions tend to change together, it is therefore difficult to interpret whether any individual parameter is responsible for the variation in total metal deposition rates. There appeared to be a slight inverse relationship between the mean relative humidity and the total metal deposition, and a positive correlation between both the mean temperature and total metal deposition and the mean total daily sunshine hours and total metal deposition.

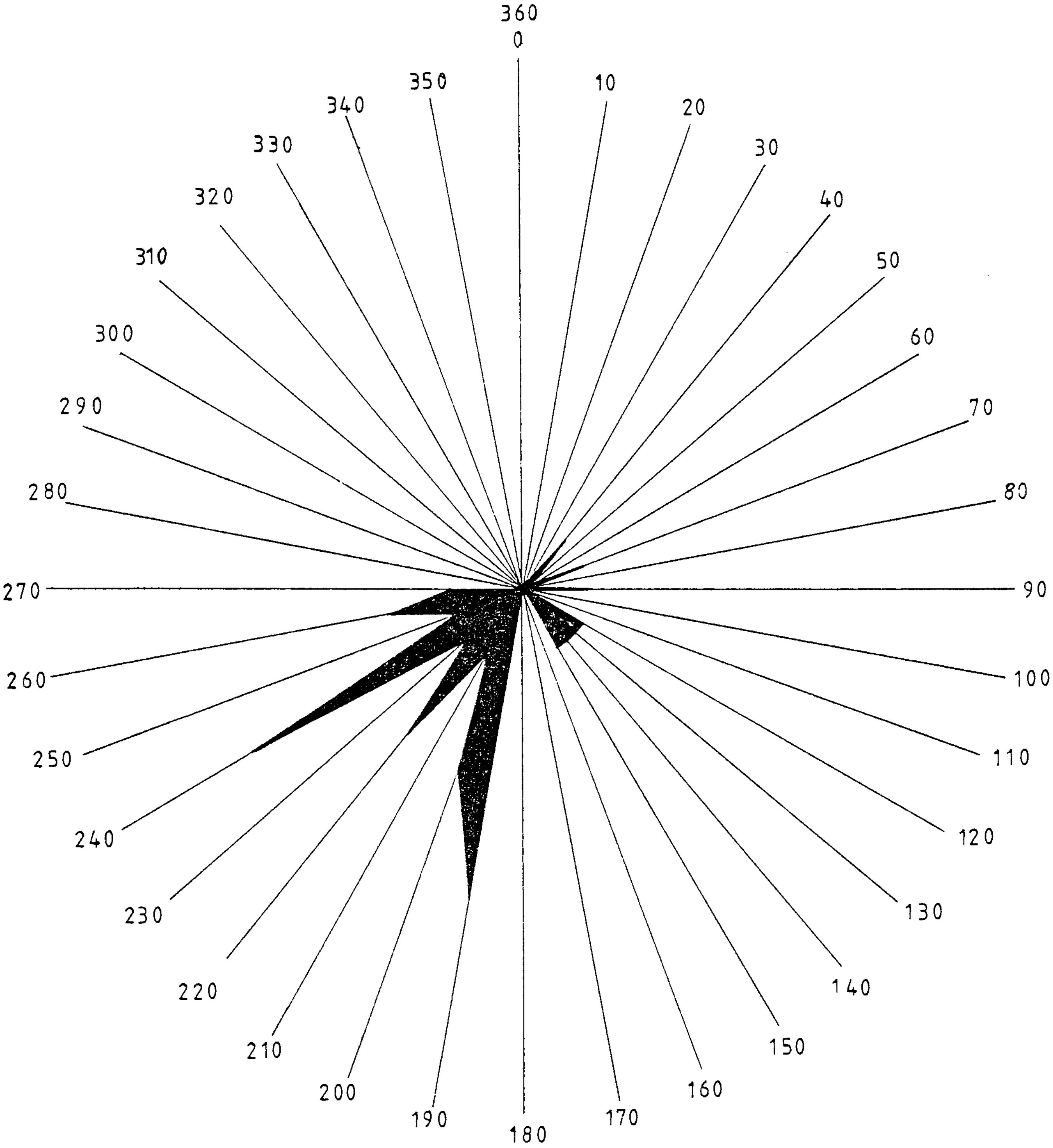


Figure 9.6 Wind rose for the period 13/09/83 to 11/10/83.

DATE	NUMBER OF DAYS							
	N	S	E	W	NE	SE	SW	NW
16/08/83	5	2	10	11	6	6	8	8
13/09/83	2	10	8	8	6	9	11	2
11/10/83	1	14	3	10	3	3	22	0
08/11/83	1	13	5	9	3	6	16	3
06/12/83	1	12	8	7	6	9	10	3
03/01/84	0	14	3	11	0	10	16	2
31/01/84	1	9	3	15	0	4	18	6
28/02/84	6	7	6	9	8	7	8	5
27/03/84	7	6	7	8	8	7	8	5
24/04/84	1	9	17	11	5	4	12	7
22/05/84	6	6	14	2	18	5	4	1
19/06/84	7	9	2	10	2	9	8	9
17/07/84	4	8	1	15	0	3	12	13

Table 9.10 Days wind in a given sector for each sampling period.

There are many possible reasons why changing weather conditions can have an influence on aerial deposition. Rainfall may wash the air masses clean and therefore less will be carried to the catchment. Higher relative humidity results in the formation of larger particles and hence a greater ability to retain particles in suspension which will eventually fall out with a greater deposition rate. With the increase in temperature the air becomes less dense, because the particle weight remains the same the heavier particles previously held will be deposited.

In addition the sunshine hours will obviously effect the temperature of the air and will therefore influence the aerial deposition as previously described.

Seasonal activity, including agricultural practices and construction activities are also dependent on the weather conditions and may therefore be partially responsible for the variation in the metal deposition rates over the year.

Wind directions are known to affect deposition rates in certain areas. From consideration of the map of the catchment area it can be seen that wind coming into the area will either pass over open countryside, i.e. from the south-west and south, or from the urban and industrial areas in the north and north-east. A clear negative correlation has been observed between the total metal deposition and the number of wind days blowing from the south-western and southern sector, with a correlation coefficient of - 0.68. This suggested cleaner, less polluted air is being blown from the south-west. A positive correlation was also seen between the total metal deposition and the number of wind days from the northern sector (r = 0.84), suggesting that more polluted air was coming in from the north, i.e.

the more industrialized areas of Birmingham and the West Midlands.

9.6.1.2 Iron

There was a high correlation between total metal deposition and iron deposition (r = 0.99) illustrating the predominance of iron in the samples. It would therefore be expected that the patterns discussed for total metal deposition would apply to that of iron.

A marked seasonal trend has been found for iron (Figure 9.7 (b)), with a peak of approximately 65 mg/m^2/28 days occurring in June and a minimum of less than 20 mg/m^2/28 days in November and January. The values were probably due to seasonal activities within the catchment. During the warmer and drier summer months maximum dust suspension from road surfaces and soils would occur. This could also be accentuated by vehicles within the catchment and the motorway. Human and agricultural activity would also be higher during the summer and this could also influence the resuspension of soils and dusts into the atmosphere (e.g. tilling of the soil). It has also been noted that the soil within the catchment area was a major source of iron (Chapter 11).

There was also a slight negative correlation (r = - 0.63) between the iron deposition and mean relative humidity, and a slight positive correlation for the total daily sunshine hours (r = 0.64).

The iron deposition rates observed within the catchment areawere well within the ranges found for other urban areas i.e. between 14 and 140 mg/m^2/28 days.

9.6.1.3 Lead

Lead deposition levels were found to be reasonably constant throughout the year (Figure 9.7 (c)) and had a mean value of 2.82 mg/m^2/28 days, with a range from 2 to less than 4 mg/m^2/28 days. This suggested a constant input of lead to the catchment area throughout the study period. The most likely source of which was vehicle emissions. It was shown in Section 7.3 that the annual vehicle flow within the catchment did not display much variation, thus confirming the observed patterns of lead deposition rates found.

It would seem reasonable to expect a relationship to exist between lead deposition rates and the number of days the wind was coming from the motorway, i.e. from the north and east. However, no such relationship was found, the probable explanation being that the deposition of lead only occurs within a very short distance from any road, usually within 30 metres (Section 5.3.2.4.2). The edge of the catchment was approximately 100 metres from the motorway, hence any effects from the motorway would not have been felt within the catchment. There was however, a slight positive correlation between the number of days the wind was coming from the north and the lead deposition rate ($r = 0.63$), suggesting that the origin of lead was from outside the area, that is, from the motorway and from Birmingham's industrialized areas, as well as from within the area itself.

9.6.1.4 Zinc

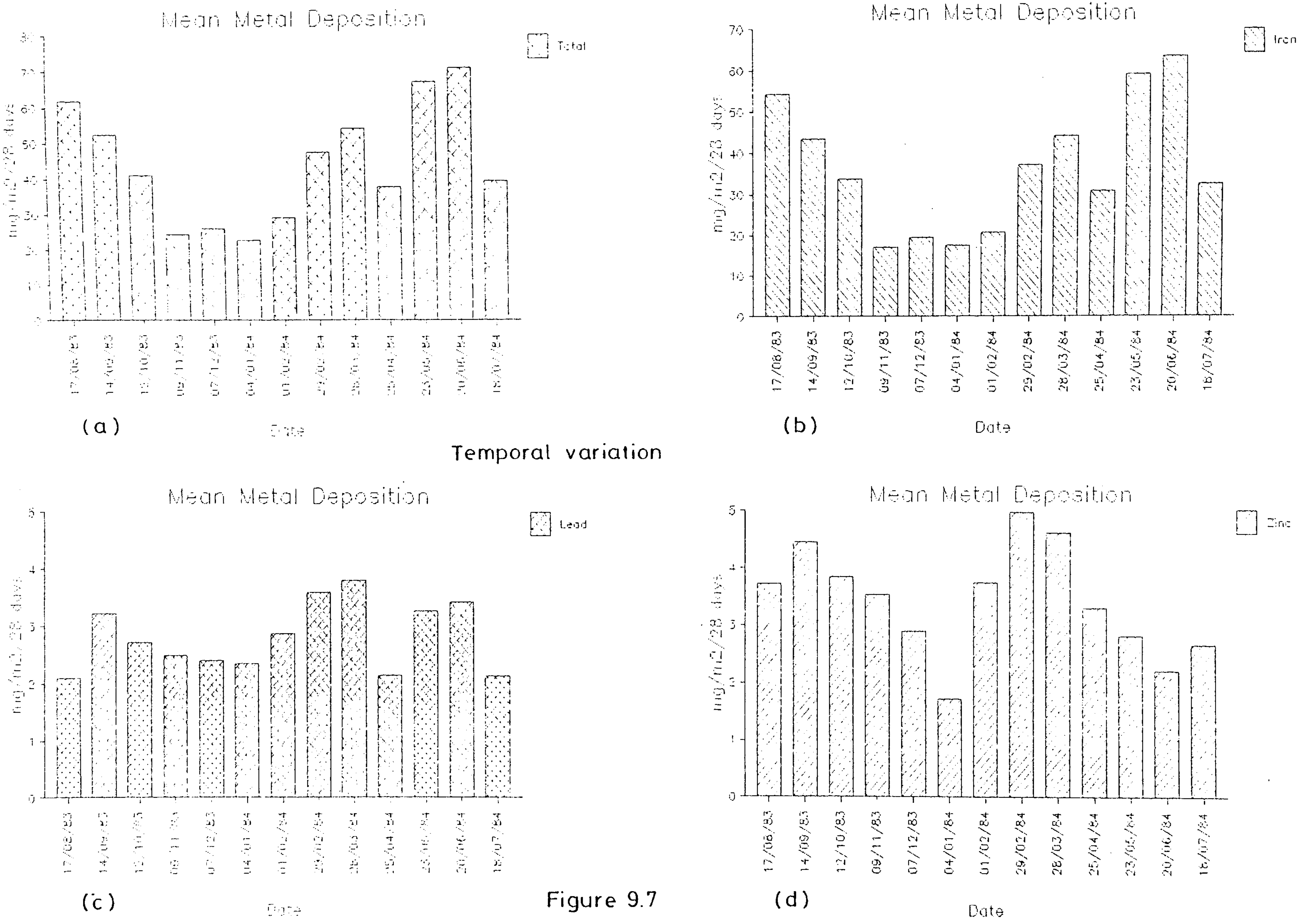
There were no distinct seasonal variations observed in the zinc deposition levels which displayed apparently random fluctuations about the mean value of 3.42 $mg/m^2/28$ days, with a range from between 1.73 and 4.97 $mg/m^2/28$ days. The highest levels occurred in February, March and September and the lowest levels in January, June and July (see Figure 9.7 (d)).

Above average deposition levels were observed during the harvesting period. It has been suggested that such agricultural practices could effect zinc deposition rates (Simmons (1985)), with the release of pesticides, fungicides and fertilizers into the atmosphere.

9.6.1.5 Copper

Copper deposition levels remained reasonably constant throughout the year with no marked seasonal variation as can be observed from Figure 9.7 (e). The average value for the year was 0.91 $mg/m^2/28$ days, with a range from 0.45 to 1.41 $mg/m^2/28$ days. The highest levels tended to occur in August and September with the lowest values in January.

The copper and zinc deposition patterns over the year displayed the same general trend, indicating a common source of the two metals. Copper and zinc have been found to occur together in other studies, and hence their fluctuations over time would be expected to follow a similar trend of behaviour with respect to each other.



Temporal variation

Figure 9.7

9.6.1.6 Chromium

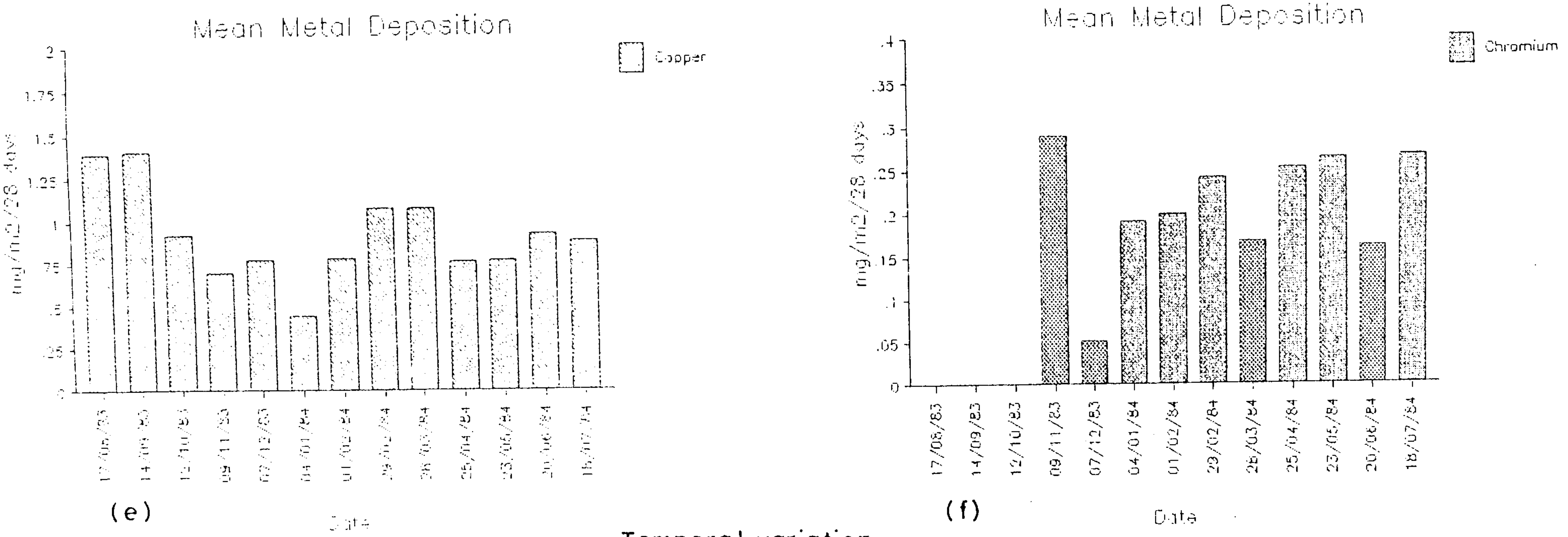
Chromium levels were observed to be low throughout the whole year (Figure 9.7 (f)) and had an average value of 0.16 mg/m^2/28 days with a range from zero to 0.29 mg/m^2/28 days. No distinct seasonal trend could be identified, the highest levels were observed during November but no chromium was detected during August, September and October. The rapid rise from zero in October to a peak of 0.29 mg/m^{2}2/28 days during November could be attributed to the onset of street salting since road salt has been identified to be a source of both chromium and nickel (Hedley and Lockley (1975)).

9.1.6.7 Nickel

Nickel levels exhibited no seasonal pattern (see Figure 9.7 (g)), the mean value for the year was 0.32 mg/m^2/28 days. Maximum levels (0.78 mg/m^2/28 days) occurred in February which may also be attributed to road salt with nickel being introduced into the atmosphere by the spray from vehicles and the prevailing meteorological conditions.

9.6.1.8 Cadmium

Cadmium depostion rates remained very low throughout the year (see Figure 9.7 (h)), with an average annual value of 0.16 mg/m^2/28 days and a range of 0.03 to 0.42 mg/m^2/28 days. However, since the maximum level observed was almost three times the mean, it would suggest that the maximum value was a spurious result, which could have been due to contamination of the sample, it was therefore disregarded in the analysis. The revised mean was then calculated to be 0.088 and a range from 0.03 to 0.15 mg/m^2/28 days was now appropriate.



Temporal variation

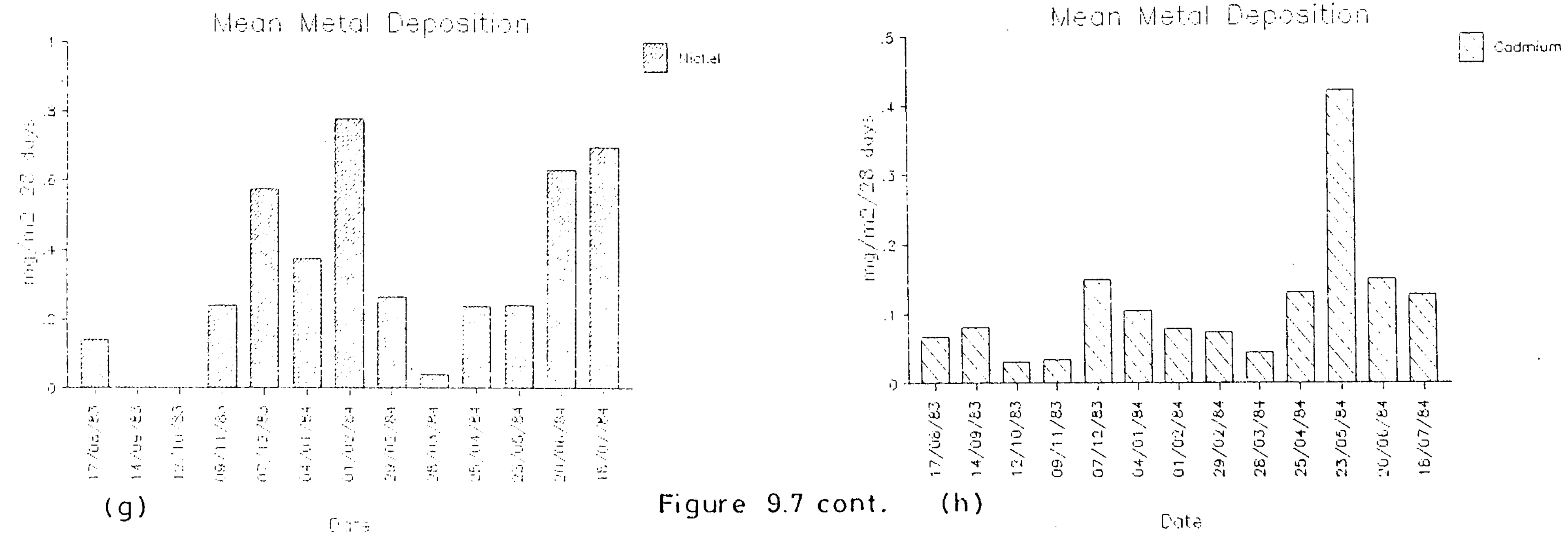


Figure 9.7 cont.

A slight positive correlation was found between the number of days the wind was blowing from the east and the cadmium deposition rates. This would suggest a source of cadmium to the east of the catchment, possibly the motorway, since cadmium has been found to be a vehicle related pollutant (Section 5.3.2.4.2).

9.6.1.9 Discussion

Few of the heavy metals studied displayed seasonal variations in deposition rates. The prominant deposition rates were those of total metal and iron, both of which were greater during the summer months. The patterns observed could be attributed to the antecedent dry period length, coupled with urban wind turbulence induced by motor vehicles. It is possible that agricultural practices could also have been a causal factor in the seasonal metal deposition rates since the spraying and harvesting of crops will introduce a greater proportion of particulates into the atmosphere which must be later deposited.

9.7 Spatial Variation in Metal Deposition

The emission of particles containing heavy metals result from many of mans activities, which include various industrial activities, local combustion, vehicles, metallurgical processes and refineries. The particles will be transported via atmospheric processes, primarily in a downwind direction, away from the source. However, rapid settling of the larger particles and concentration dilution, through dispersion of suspended particles, suggest that deposition rates should decline with increasing distance downwind.

In urban areas where complex patterns of sources exist it would be expected that deposition would display high spacial variability, ranging from peak deposition levels in source 'hot spot' areas, to near background levels in low density open areas. Conversely, for rural areas deposition is likely to display less spatial variability.

Theoretical consideration suggests, therefore, that a declining relationship between distance from source and deposition rate should exist which has correspondingly been found to be the case by numerous researchers (e.g. Turner et al (1980), Beavington (1977), Roberts et al (1976), and Little and Martin (1974)).

Lead deposition in the vicinity of roads has been observed to follow a similar pattern of decrease in concentration with distance (Crump and Barlow (1982) and Little and Wiffen (1978)). Cadmium deposition has also been noted to decrease with distance from roads (Lagerwerff and Specht (1970)). In many studies the exponential decay has been found to be a good representation for the distance decline relationship.

In rural areas source impact can be detected at distances up to 30 km from the source. However, in urban areas background levels are generally elevated and display more spatial variability, therefore the source impact attributable to an individual source becomes indistinguishable from the background at distances within a few kilometers radius from the source. Even in close proximity to sources, levels at or near background levels can still be observed, the degree of spatial variability in deposition increases with proximity to the source.

9.7.1 Spatial Variation in Metal Deposition in Chelmsley Wood

The mean metal deposition for each deposit cannister location was calculated for the entire sampling period and the results are presented in Table 9.11 and Figure 9.8. From consideration of the Table and Figure it can be seen that the spatial distribution of atmospherically derived pollutants were not homogenous across the catchment.

9.7.1.1 Total Metals

Figure 9.8 (a) illustrates the spatial variation in the total heavy metal deposition over the catchment, from which it can be seen that there were a couple of large fluctuations about the mean value of 46 mg/m^2/28 days. The fluctuations occurred at location 19, where the concentrations were approximately twice the mean value, and at location 22, with values approximately half the mean value. However, it was not possible at this point to supply an explanation for the observed fluctuations, the reason being that the total metals are a summation of all the metals studied and will hence mask any individual variation within the metals. At all other locations only slight variation was observed of approximately 15 mg/m^2/28 days about the mean.

LOCATION	IRON	LEAD	ZINC	COPPER	CHROMIUM	NICKEL	CADMIUM	TOTAL
1	28.04	3.33	3.08	0.75	0.17	0.53	0.095	35.99
2	41.38	7.22	3.85	1.00	0.16	0.54	0.106	54.26
4	32.89	3.14	3.65	1.21	0.12	0.37	0.137	41.52
5	22.67	2.75	2.32	0.60	0.18	0.45	0.145	29.11
6	21.30	2.60	3.81	0.83	0.03	0.25	0.003	28.81
7	30.68	2.27	3.07	0.66	0.13	0.14	0.120	37.07
8	35.63	2.34	3.79	0.95	0.18	0.30	0.155	43.35
9	23.81	2.63	2.40	0.64	0.15	0.18	0.152	29.96
12	48.64	3.14	2.99	0.65	0.27	0.29	0.077	56.06
14	51.10	1.34	4.19	1.29	-	-	0.074	58.00
15	28.80	3.71	4.22	1.10	0.15	0.48	0.148	38.60
16	40.87	2.14	3.37	0.98	0.20	0.41	0.070	48.04
18	53.94	2.72	4.12	1.35	-	-	0.081	62.22
19	95.58	2.07	2.72	1.71	-	-	0.053	102.13
21	42.27	2.36	3.73	1.02	0.15	0.42	0.148	50.11
22	16.41	1.08	2.39	0.95	0.03	0.18	0.035	21.07
Mean	38.37	2.80	3.36	0.98	0.12	0.28	0.099	46.02
Std.Dev.	18.87	1.36	0.66	0.30	0.08	0.19	0.046	19.10

Table 9.11 Spatial variation of metal deposition in Chelmsley Wood. (mg/m^2/28 days)

9.7.1.2 Iron

As would be expected the spatial variation of iron closely followed that of the total metal deposition due to the predominance of iron in all samples (see Figure 9.8 (b)). Once again location 19 has an extremely high level of approximately 96 mg/m^2/28 days. It is possible that the observed high concentration may have been due to the actual siting of the cannister, since as a result of vandalism the cannister had to be removed from the lamppost and placed at a lower level on top of a porch. Soil particles may therefore have become resuspended in the close vicinity and caught within the cannister. Location 22 experienced low iron deposition with values falling to around 16 mg/m^2/28 days. Similarly all other locations displayed deposition rates within the value of approximately 15 mg/m^2/28 days, whilst locations 12, 14 and 18 displayed above average deposition rates.

9.7.1.3 Lead

Lead deposition rates tended to be more uniform across the catchment (Figure 9.8 (c)) with few locations experiencing any significant variation from the mean (2.8 mg/m^2/28 days). Higher lead deposition rates were observed at locations 1, 2, 4, 12 and 15, all of which were on the outer boundary of the area. The cannister with the highest lead deposition rate was at location 2, with a mean value of 7.2 mg/m^2/28 days, and had the closest location to the motorway. This location experienced considerably high levels and increased the overall mean substantially.

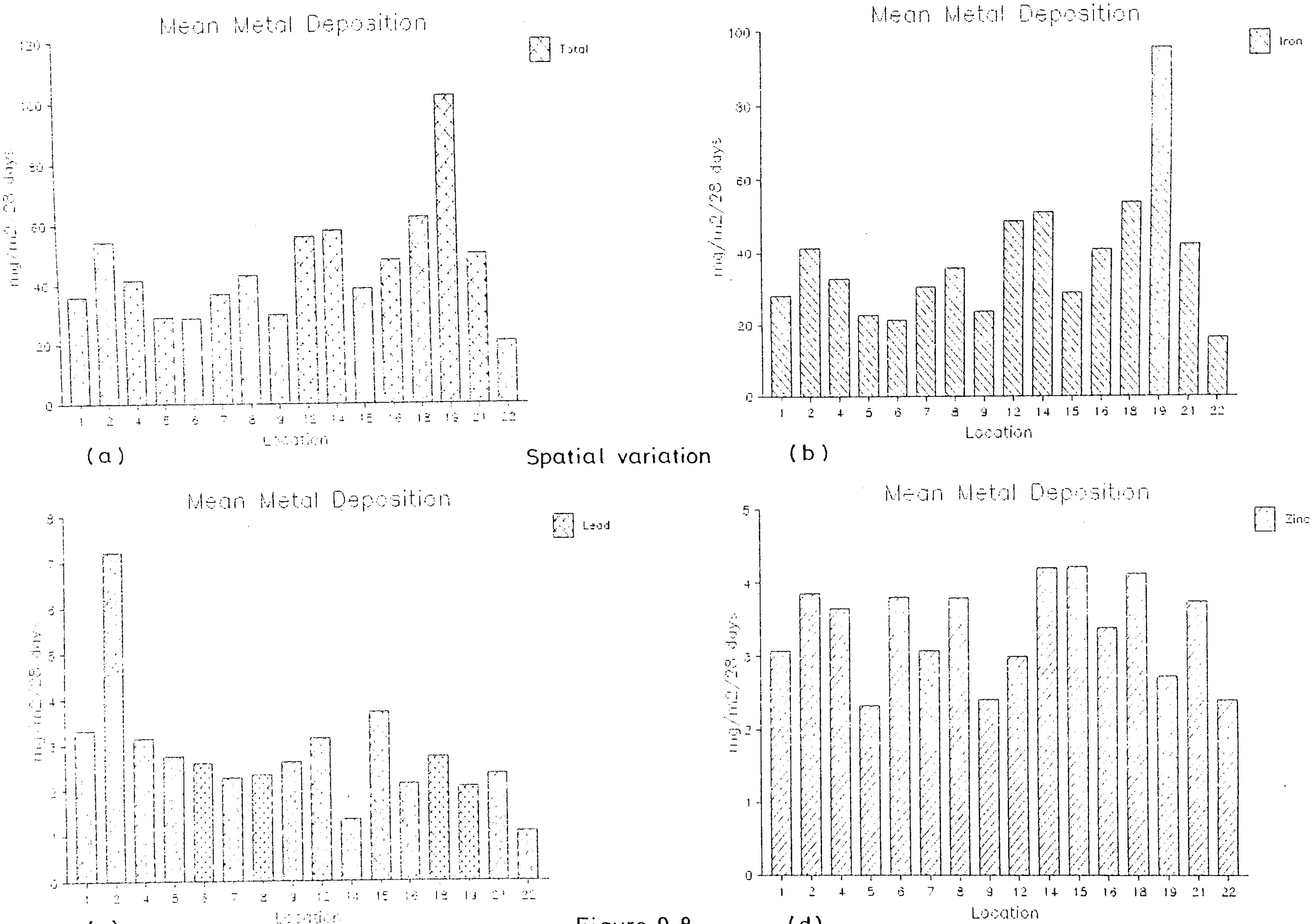
The lowest lead deposition rates were observed at locations 22 and 14, with values of 1.08 and 1.34 mg/m^2/28 days respectively. The latter cannisters were located within the centre of the catchment and were sheltered from the influence of the motorway and major roads. At all other locations the lead deposition rates were within 0.8 mg/m^2/28 days of the mean.

9.7.1.4 Zinc

Zinc deposition rates remained fairly constant across the entire catchment, with no observed large fluctuations from the mean value of 3.35 mg/m^2/28 days, see Figure 9.8 (d). Slightly higher zinc deposition rates were observed at locations 2, 4, 6, 8, 14, 15, 18 and 21 and lower than average deposition rates at locations 5, 9 and 22. However, no distinct pattern was identifiable, but it would appear that higher zinc deposition rates were generally found within the southern sector of the catchment, with lower values within the northern sector. The source of zinc within the southern sector could be attributable to agricultural practices.

9.7.1.5 Copper

The spatial distribution of copper deposition is illustrated in Figure 9.8 (e). The mean copper deposition was 0.98 mg/m^2/28 days and the maximum rates were found at locations 19 and 18 with values of 1.71 and 1.35 mg/m^2/28 days respectively. No distinct spatial variability emerged, but once again as with zinc, higher levels tended to occur within the southern sector of the catchment. However, the majority of copper deposition rates were close to the average value.



Spatial variation

Figure 9.8

9.7.1.6 Chromium

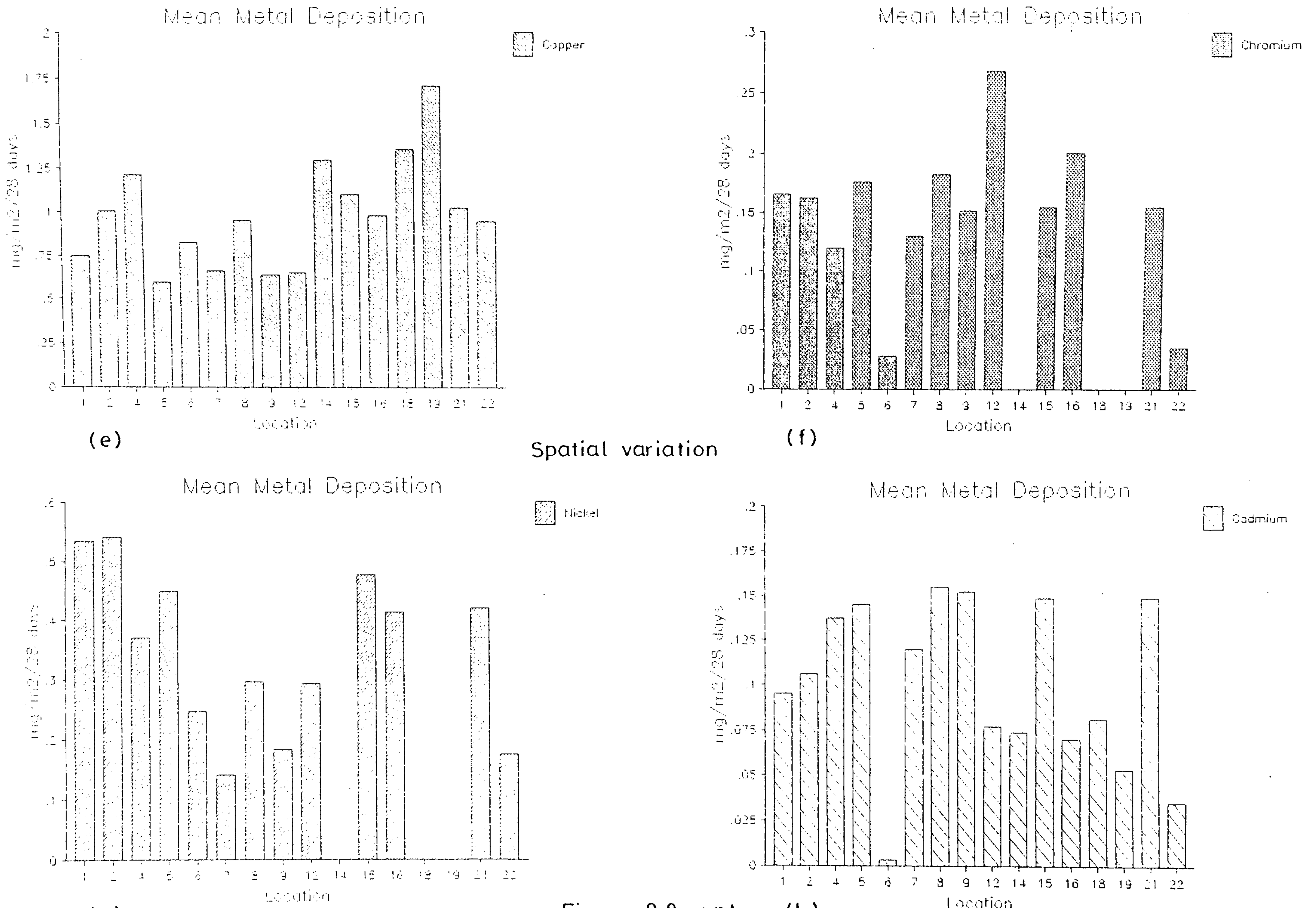
Chromium deposition rates varied considerably throughout the catchment (see Figure 9.8 (f)) but levels observed were generally low. The maximum chromium deposition rate was observed at location 12 (0.27 $mg/m^2/28$ days) and little or none was found at locations 6, 14, 18, 19 and 22. No consistent pattern could be identified and therefore irregularities may have been due to local effects within the area such as micro-climates, topography or sheltering due to buildings etc..

9.7.1.7 Nickel

As with chromium, nickel deposition displayed large fluctuations across the catchment (Figure 9.8 (g)). The greatest levels were observed at locations 1, 2, 5 and 15 with deposition rates of 0.53, 0.54, 0.45 and 0.48 $mg/m^2/28$ days respectively. All of the latter cannisters were located around the periphery of the area and may therefore be source related to road salting of the major priority routes around the periphery of the area (Figure 7.4). This hypothesis is partly substantiated by the fact that zero nickel levels were observed at locations 14, 18 and 19, all of which were located within the interior of the catchment, where no street salting occurred. Therefore a decline in nickel deposition was observed with distance from the exterior of the catchment to the interior.

9.7.1.8 Cadmium

Cadmium deposition rates were low throughout the catchment and tended to fluctuate randomly, see Figure 9.8 (h). However, as with nickel, lower than average cadmium levels were seen to predominate within the centre of the catchment, with higher levels around the periphery, which could be traffic related.



(e) (f) (g) (h)

Spatial variation

Figure 9.8 cont.

9.7.1.9 Discussion

Many of the metal deposition rates did not show any identifiable spatial variation, which may have been due to localized conditions such as micro wind patterns, topography and the sheltering by buildings.

One location, location 2, consistently exhibited higher than average metal deposition rates for all of the metals studied. This may have been due to the fact that the cannister location was the closest to the motorway, (location 1 was sheltered by the motorway embankment) thus suggesting a metal input into the catchment from the motorway environment.

Location 22 had consistently lower than average metal deposition rates and was located within the interior of the catchment, at a reasonable distance from any major roads or the motorway.

In order to investigate the hypothesis that the motorway and distance towards the centre of the catchment may have had an influence on the metal deposition rates, distance contour maps were drawn and are discussed in the following Section.

9.8 Metal Deposition with Distance from Motorway

Contour lines were drawn at 100 m intervals across the catchment area, parallel to the motorway (see Figure 9.9). The deposit cannisters lying within each 100 m boundary were noted together with the corresponding average deposition rates. The mean metal deposition for each band width were then calculated and the results are presented in Table 9.12.

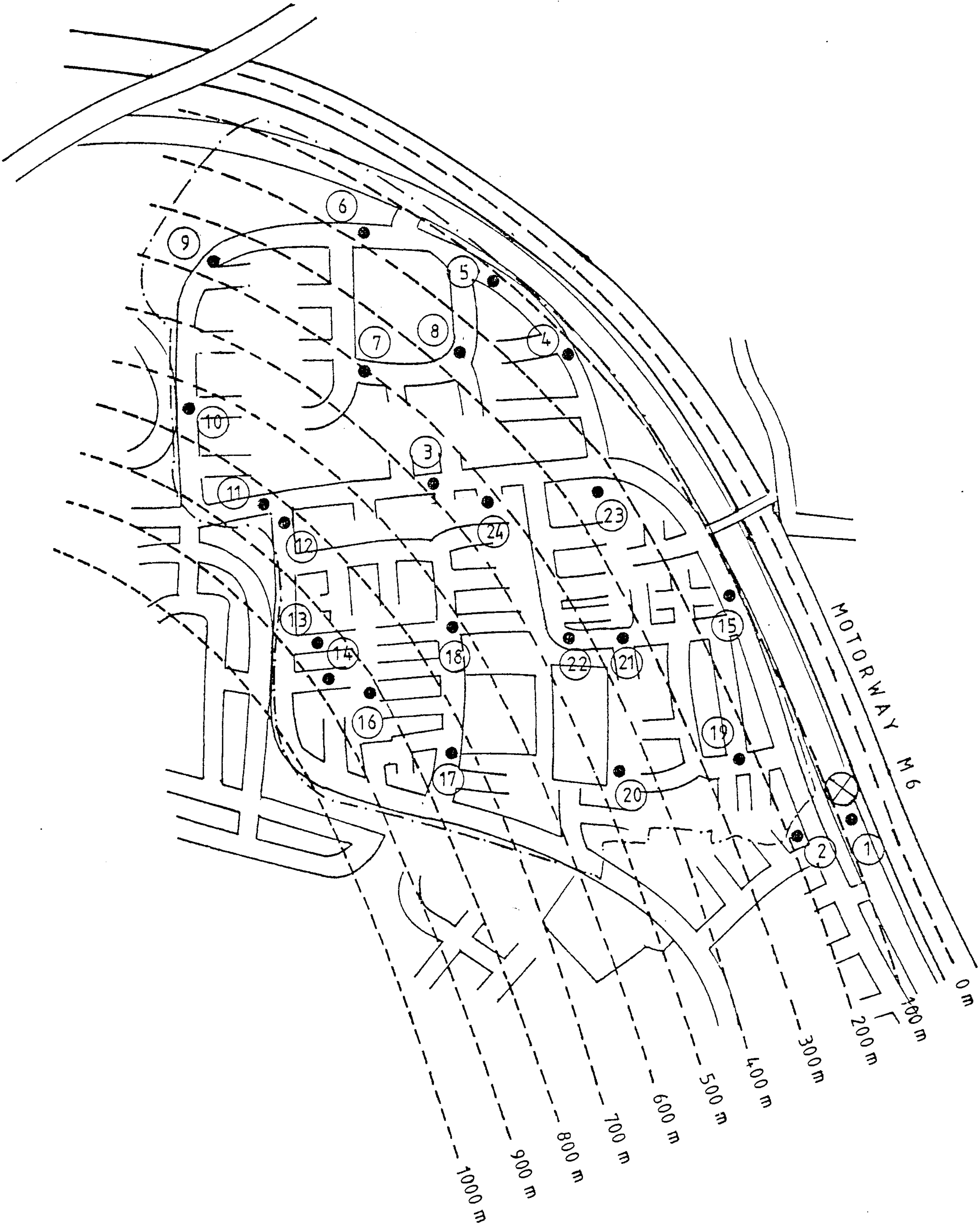


Figure 9.9 Location of deposit cannisters with distance from motorway.

From consideration of the Table it can be seen that there was no pronounced distance decline relationship in the metal concentrations with distance from the motorway. The lack of any distance decline relationship may have been due to the fact that the experimental catchment area was of such a distance from the motorway (greater than 100 m) that no direct effect from the motorway would have been experienced.

However, there was a marked decline in the metal deposition between the 400 and 600 m band, and levels generally declined with distance up to 450 m and then increased again. The centre of the experimental catchment was located approximately 400 to 500 m from the motorway and may therefore be a contributory factor since the area may have been relatively sheltered from any outside influences.

Iron levels increased rapidly from 0 to 300 m and then fell dramatically, this could have been due to the fact that the band width area was exposed, and that air travelled from outside the area passed over open agricultural land, bringing with it soil and other particles. Lead levels generally fell with distance and zinc followed a similar pattern to lead but more subdued. Copper and cadmium were fairly constant and chromium and nickel fell to a distance of 500 to 600 m and then increased rapidly.

9.9 Metal Deposition with Distance from Centre of Catchment

As in Section 9.8 contour lines were drawn at 100 m intervals but this time from the centre of the catchment as shown in Figure 9.10. The deposit cannisters lying within each band width were recorded together with the corresponding average deposition rates. The mean metal deposition for each band width are presented in Table 9.13.

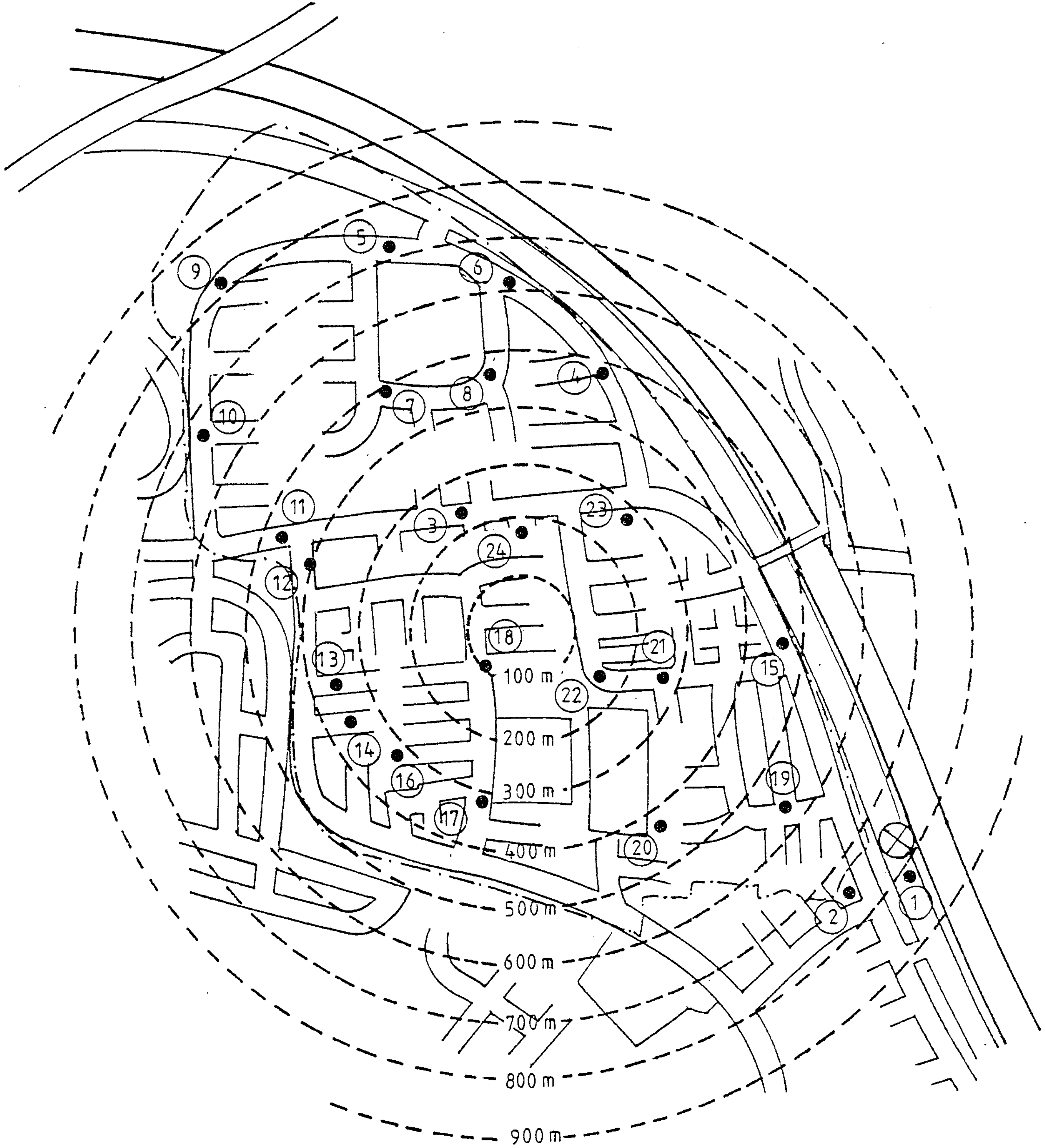


Figure 9.10 Location of deposit cannisters with distance from centre of catchment.

BAND WIDTH (m)	Mean metal deposition mg/m^2/28 days							
	Fe	Pb	Zn	Cu	Cr	Ni	Cd	Tot
0 - 100	24.67	2.96	3.44	0.786	0.097	0.390	0.049	64.79
100 - 200	31.43	4.20	3.51	0.978	0.153	0.459	0.134	40.87
200 - 300	65.60	2.20	3.25	1.329	0.183	0.297	0.104	72.74
300 - 400	32.25	2.42	3.01	0.774	0.146	0.248	0.140	39.05
400 - 500	16.41	1.08	2.39	0.948	0.035	0.176	0.035	21.07
500 - 600	53.94	2.72	4.12	1.350	-	-	0.081	62.22
600 - 700			NO DATA					
700 - 800	48.64	3.14	2.99	0.650	0.268	0.293	0.077	56.06
800 - 900	45.98	1.74	3.78	1.140	0.201	0.413	0.072	53.01
900 - 1000			NO DATA					

Table 9.12 Mean metal deposition with distance from motorway.

BAND WIDTH (m)	Mean metal deposition mg/m^2/28 days							
	Fe	Pb	Zn	Cu	Cr	Ni	Cd	Tot
0 - 100	53.94	2.72	4.12	1.350	-	-	0.081	62.22
100 - 200	16.41	1.08	2.39	0.948	0.035	0.176	0.035	21.07
200 - 300	42.27	2.36	3.73	1.022	0.155	0.420	0.148	50.11
300 - 400	46.87	2.21	3.52	0.975	0.156	0.235	0.074	54.03
400 - 500	32.44	3.06	3.89	1.087	0.153	0.382	0.146	41.16
500 - 600	63.13	2.17	2.89	1.184	0.130	0.141	0.086	69.60
600 - 700	21.30	2.60	3.81	0.827	0.028	0.247	0.003	28.81
700 - 800	32.02	4.98	3.08	0.802	0.169	0.495	0.125	41.68
800 - 900	25.92	2.98	2.74	0.693	0.159	0.358	0.123	32.97

Table 9.13 Mean metal deposition with distance from centre of catchment.

No distinct pattern for all the metals emerged. However, there was a decrease in metal deposition within the 100 to 200 m sector, which was probably due to the sheltering effects. Iron peaked between the 500 and 600 m boundary and most cannisters within this band were located around the periphery of the area, once again adjacent to open spaces. Lead deposition generally increased with distance from the centre of the catchment to the motorway, as did zinc. Copper, chromium and cadmium were fairly uniform with nickel showed random fluctuations.

Since the bands encompass both the perimeter and the central cannisters it was difficult to distinguish a particular pattern, therefore contour lines were redrawn from the edge of the catchment boundary (Figure 9.11). The average deposition rates within these boundaries are given in Table 9.14.

Iron and nickel deposition rates gradually increased within the first 200 m and fell with further distances from the catchment boundary. Zinc increased from the catchment boundary and reached a maximum within the centre of the catchment. Lead levels were high around the periphery of the area and fell within 200 m, thereafter a rise in value was observed. It would appear that the patterns were related to the location of the major roads within the area. Copper deposition was fairy uniform within each band with chromium and cadmium dropping towards the centre of the catchment.

Unfortunately no overall distinct pattern could be determined and therefore deposition rates could be dependent upon very localized conditions, masking any effects that may be attributed to the distance from the catchment boundary.

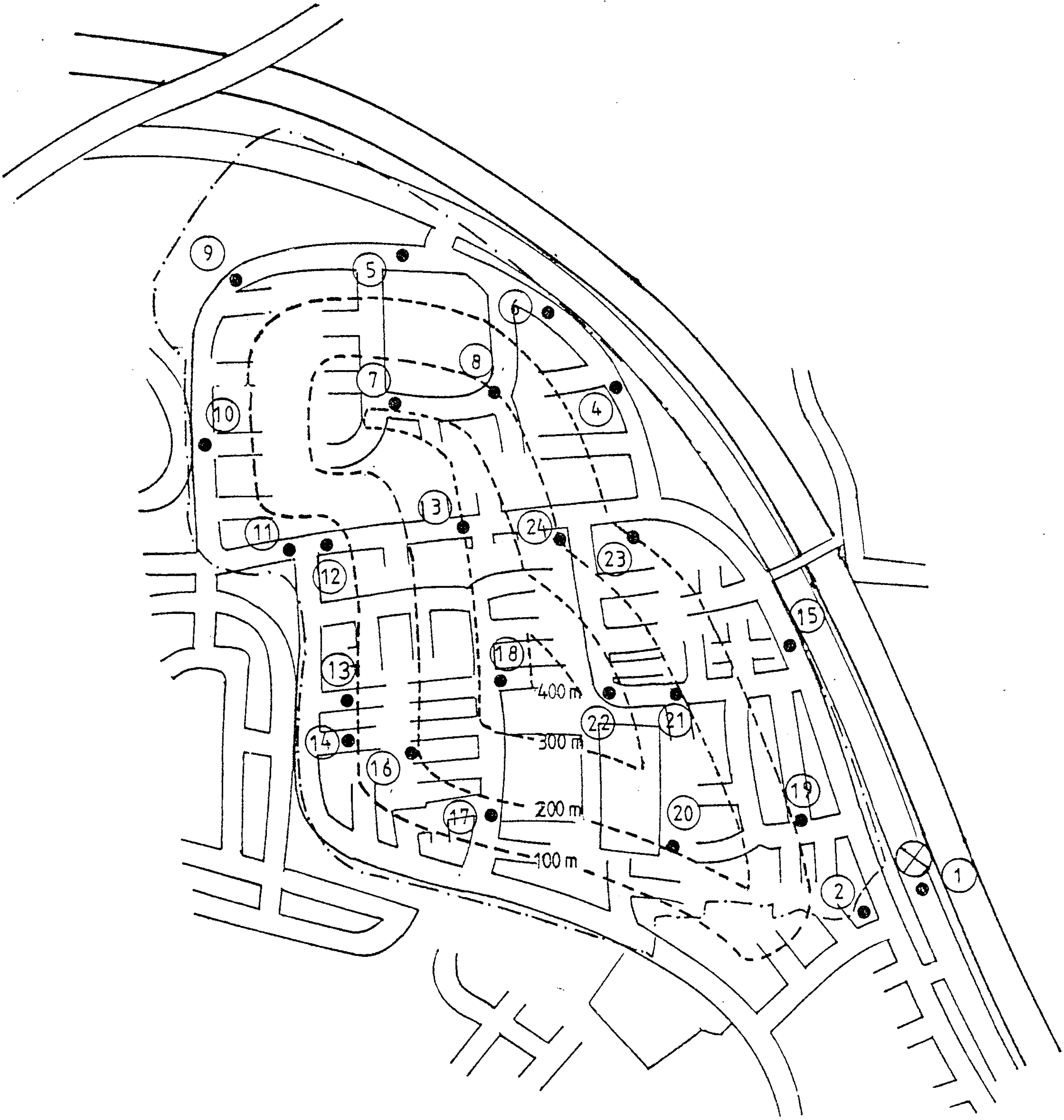


Figure 9.11 Location of deposit cannisters with distance from the catchment boundary.

BAND WIDTH (m)	Mean metal deposition $mg/m^2/28$ days							
	Fe	Pb	Zn	Cu	Cr	Ni	Cd	Tot
0 - 100	38.12	3.40	3.23	0.943	0.153	0.327	0.102	46.27
100 - 200	42.53	1.94	3.78	1.075	0.128	0.435	0.134	49.79
200 - 300	36.47	3.45	4.94	0.840	0.142	0.280	0.134	62.12
300 - 400	35.17	3.26	5.31	1.150	0.017	0.088	0.098	41.64

Table 9.14 Mean metal deposition with distance from catchment boundary.

9.10 Concluding Remarks

From previous and contemporary studies of deposition, it is clear that metal deposition rates are strongly influenced by anthropogenic activity (in particular, industralized dischages of particulates into the atmosphere) and deposition rates follow the general trend of remote < rural < urban concentrations.

Aerial deposition has been shown to follow an exponential decline with increasing distance from the source (Simmons (1984)). Spatial variability is greatest in close proximity to sources, where it has been shown that even within a few hundred metres of large sources of metals, deposition more typical of background levels may be observed.

Since there was no singular individual source of metal pollution within or close to the study area, except for possibly the M6 motorway, it was difficult to verify the concept of an exponential decay in concentration with distance from source, or to ascertain any pattern of spatial variability for aerial deposition. However, there was some indication of metal decline (especially lead) with distance from the motorway, but further work, incorporating a greater density of deposit cannisters, at varying distances from the motorway would be required to verify this hypothesis.

Even though the spatial variability of metal deposition over the catchment area was not significant, local variations were often observed. The local variations may have been due to localized conditions, such as increased intensity of land use activities (e.g. shopping and vehicles) causing greater displacement and resuspension of solids within the atmosphere.

The open and more exposed areas to the south-western sector were subject to cleaner, less polluted air coming in from the countryside, whilst the northern sector, which was closer to urban areas, more likely to receive pollutants.

The reduced concentrations of metal pollutants found in Chelmsley Wood, compared to other urban sites is probably natural rather than anthropogenically induced. Industrial stacks and other point emitting sources were not present either in the immediate district or surrounding vicinity (i.e within 1 km radius).

Metal deposition values given in this section were obtained over the whole catchment area during the sampling period. However, the total input to the catchment will not necessarily be reflected within the stormwater runoff, since some deposition will have fallen onto permeable areas, such as gardens and open grassland and a large proportion been lost into the soil store. Deposits that fall directly onto impervious surfaces, such as roads and roofs, would have been the fraction that would predominantly have been transported directly into the sewer system. Therefore the results presented in this Section were the 'potential' metal source from aerial deposition for the catchment area. The proportion of these quantities that were finally realized within the stormwater runoff, is at this stage, unknown.

CHAPTER 10

ROAD SEDIMENT HEAVY METAL CONTENT

10.1 Introduction

Heavy metals in road sediments were discussed in Section 5.3.2.3. It should be stressed at this point that the sampling of deposited dust is open to critisism. The significance of the individual results mean nothing more than the level of metal in a given place at the time of sampling (Archer and Barratt (1976)). The ignorance of the history of the sample means that it is not known whether a given concentration had been reached over a period of hours, days, months or decades. Moreover local incidents may cause abnormally high concentrations, which are not representative of the general area. It can therefore be argued that no great significance should be accorded to individual samples, but all should be bulked together to give an average figure for the whole catchment (this method was adopted in the computer model described in Chapter 14). It is also possible to calculate the metal proportions within the samples, the resulting values will then be independent of absolute concentrations of the metals observed. Both approaches have been used in this study.

In relation to the Chelmsley Wood study, there was a further problem in that the majority of samples were collected from the gutter, where sufficient sediment could be sampled. It has been shown in the literature that sediment tends to accumulate at this point and greater loadings are found. As a result a sample from any one point would therefore not be representative of the whole length of road or gutter. However, it does provide information on the concentration of pollutants present at any one location.

10.2 Heavy Metals in Road Sediments from Chelmsley Wood

Road surface sediments were collected from the Chelmsley Wood catchment as discussed in Section 8.3. Total concentrations of iron, lead, zinc, copper, chromium, nickel and cadmium within the samples were determined.

Initially samples were taken once every two weeks at 24 locations, but later during the sampling programme, the number of sampling sites was halved in order to reduce the work load and to coincide with deposit cannister replacement.

The average metal concentration for each sampling event were calculated and the results are given in Table 10.1. An overall summary of the data, indicating the mean metal concentrations is presented in Table 10.2.

The heavy metal concentrations observed within the road sediment samples in Chelmsley Wood were seen to be comparable with contemporary studies from other urban/residential areas (Tables 5.7 and 5.8). However, the minimum values obtained were greater than those obtained for comparable sites and in some cases by several orders of magnitude (e.g. iron 1400 mg/kg compared with 14440 mg/kg). The maximum levels observed tended to display better agreement with the maximum levels obtained from other investigations.

DATE	Fe	Pb	Zn	Cu	Cr	Ni	Cd	Tot
26/07/83	18915.80	974.23	284.84	120.97	63.88	45.84	2.01	20407
09/08/83	25505.70	1165.56	459.50	142.79	56.11	96.04	2.19	27425
23/08/83	25289.70	954.40	444.81	133.40	40.84	43.63	2.57	26909
05/09/83	27008.80	1123.13	483.85	147.03	49.60	19.63	2.77	28835
26/09/83	22745.30	933.37	533.33	114.33	47.17	34.16	2.43	24410
12/10/83	14440.10	499.87	390.83	122.72	49.11	40.37	1.18	15544
09/11/83	16463.00	630.84	473.41	107.30	50.68	37.01	1.18	17763
07/12/83	24627.30	1455.56	532.03	140.97	62.16	49.66	3.89	26872
04/01/84	17409.90	904.50	429.50	124.09	45.64	30.86	3.06	18947
01/02/84	21547.70	1138.18	534.22	139.36	65.45	51.67	2.69	23479
29/02/84	19781.60	807.09	455.82	132.36	61.59	41.80	1.95	21282
28/03/84	15734.20	1005.91	406.27	131.09	49.59	30.45	3.41	17361
25/04/84	21190.00	1068.18	400.27	115.95	49.18	37.12	0.99	23512
20/06/84	20443.40	1522.73	612.82	147.14	62.54	39.52	3.23	22831
18/07/84	22530.20	1478.64	520.86	146.68	65.14	44.65	3.30	24789
Mean	20943.00	1061.00	466.00	132.00	54.61	42.85	2.52	22699
Std.dev.	3689.60	288.88	76.44	13.08	7.90	16.25	0.88	39082

Table 10.1 Mean road sediment concentrations for each sampling event (mg/kg).

Metal	Min.	Max.	Mean
Iron	14440	27009	20943
Lead	500	1522	1061
Zinc	285	613	466
Copper	107	147	132
Chromium	40.84	65.45	54.61
Nickel	19.63	96.04	42.85
Cadmium	0.99	3.89	2.52
Total	15544	28835	22699

Table 10.2 Mean road sediment metal concentrations and ranges (mg/kg).

In particular it can be seen that the metal concentrations of zinc, copper, nickel and cadmium found in this study were comparable with those obtained by Harrison (1979) in Lancaster. This may have been due to the fact that the sites had similar characteristics and it may have also be attributable to the use of aqua regia acid digestion procedure which was employed for both investigations. The values of concentrations of lead found in Chelmsley Wood were comparable with values obtained by Solomon and Hartford (1976) for Urbana, USA. The mean iron concentration observed within the Chelmsley Wood catchment was also seen to be comparable with those found in Chilwell Gardens by Harrop (1984).

From consideration of Tables 5.8 and 10.2 it can be seen that the majority of metal concentrations found were within the range normally associated with motorway surface sediments. The average iron concentration of 20943 mg/kg was typical of a motorway surface sediment, a similar comment applies for copper and cadmium. The levels of zinc were, however, above those quoted for motorway sediments, suggesting an additional source of zinc other than that from normal vehicular inputs. The source may have been from the soil and/or local agricultural practices. Other possible sources may have been the concentration effect of previous runoff events or direct anthropogenic inputs into the catchment.

In conclusion therefore, the metal concentrations observed for the road sediments in Chelmsley Wood fell within or above the ranges quoted for motorway sediments, particularly for iron and zinc, indicating potential metal inputs from sources other than vehicles. An additional explanation for the elevated metal levels over those found in the literature is the variation in analytical methods employed in the various studies to determine the metal concentrations within the sediments. Ideally only the studies which used identical acid digestion and analytical procedures should be compared with the results from this study since comparison of results using different techniques may not be strictly valid.

10.2.1 Metal Proportions

The proportion of each metal to the total metals, in each sample was calculated and expressed as a percentage. The mean of the proportions are presented in Figure 10.1 and Table 10.3.

As with the deposit cannister samples, iron was seen to predominate within all samples throughout the year, with an average percentage of 92% (compared with 72% for the deposit cannisters), and ranged between 86 and 94%. The lowest iron proportion was observed in January (as in the deposit cannisters), which was probably due to de-icing activity. The contamination from the salt used may have caused an increase in concentration of some of the other metals hence forcing the overall proportion of iron to decrease.

As iron was dominant in all of the samples and tended to mask the variations within the other metals, the proportions were calculated excluding the metal iron. The resulting mean values for these non-ferrous metals are shown in Figure 10.2 and Table 10.4.

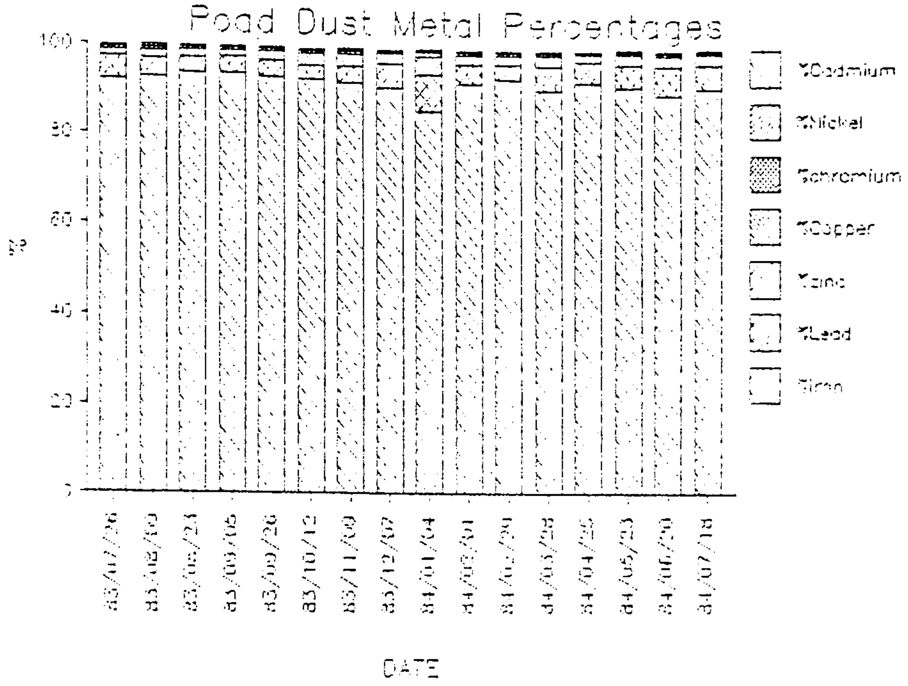


Figure 10.1 Road dust metal percentages including iron.

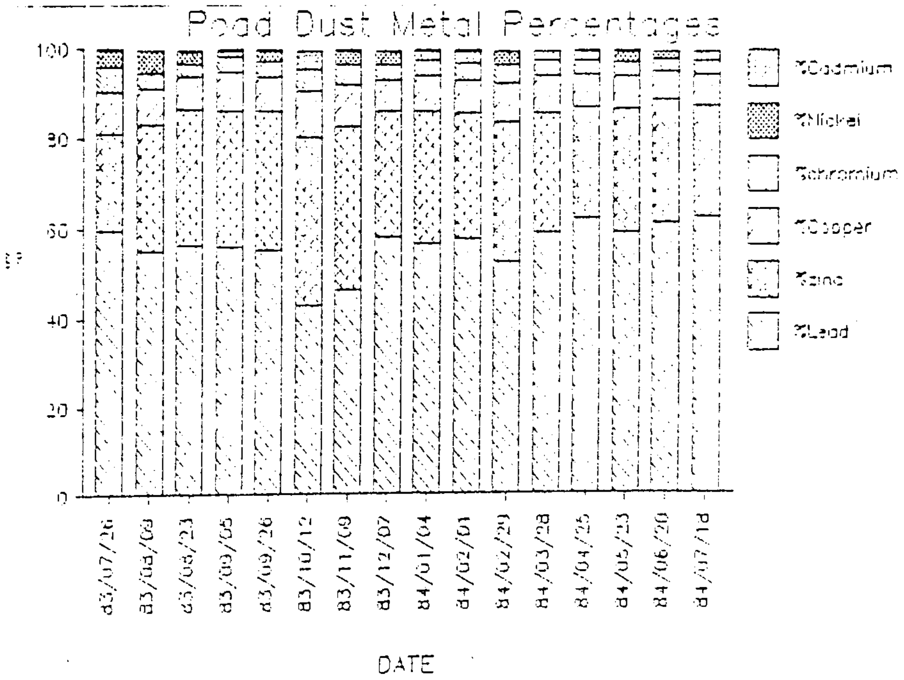


Figure 10.2 Road dust metal percentages excluding iron.

Date	Fe	Pb	Zn	Cu	Cr	Ni	Cd
26/07/84	92.00	5.20	1.52	0.65	0.33	0.24	0.006
09/08/83	92.88	4.16	1.78	0.52	0.19	0.43	0.003
23/08/83	93.90	3.59	1.75	0.41	0.15	0.16	0.005
05/09/83	93.99	3.56	1.67	0.51	0.18	0.06	0.004
26/09/83	93.33	3.77	2.08	0.46	0.19	0.14	0.004
12/10/83	93.00	3.08	2.53	0.76	0.33	0.25	0.002
09/11/83	92.09	3.84	2.82	0.66	0.32	0.23	0.001
07/12/83	91.11	5.71	2.16	0.53	0.24	0.19	0.011
04/01/84	85.77	8.52	4.01	1.03	0.30	0.31	0.020
01/02/84	92.07	4.68	2.14	0.57	0.27	0.21	0.006
29/02/84	93.08	3.70	2.11	0.60	0.28	0.19	0.005
28/03/84	90.80	5.57	2.37	0.74	0.28	0.17	0.015
25/04/84	92.65	4.60	1.83	0.51	0.21	0.16	0.004
23/05/84	91.61	5.18	2.15	0.61	0.23	0.17	0.014
20/06/84	89.79	6.43	2.67	0.63	0.26	0.16	0.008
18/07/84	90.99	5.76	2.18	0.59	0.26	0.18	0.008
Mean	91.80	4.83	2.23	0.61	0.25	0.20	0.007
Std.dev.	2.09	1.38	0.59	0.14	0.05	0.08	0.005

Table 10.3 Ferrous metal proportions within road sediments (%).

Date	Pb	Zn	Cu	Cr	Ni	Cd
26/07/83	59.79	21.25	9.24	5.67	3.85	0.17
09/08/83	55.29	27.89	7.89	3.57	5.17	0.14
23/08/83	56.55	30.09	7.10	2.80	3.22	0.19
05/09/83	56.35	30.08	8.62	3.39	1.31	0.21
26/09/83	55.42	30.89	7.66	3.35	2.48	0.17
12/10/83	42.96	37.41	10.46	4.93	4.07	0.12
09/11/83	46.35	36.35	9.53	4.34	3.32	0.09
07/12/83	58.30	27.90	7.01	3.58	2.90	0.25
04/01/84	57.02	29.14	8.15	3.42	2.01	0.22
01/02/84	58.01	27.76	7.34	3.79	2.91	0.15
29/02/84	52.58	31.32	8.58	4.36	2.96	0.16
28/03/84	59.30	26.68	8.42	3.32	1.98	0.25
25/04/84	62.26	24.92	7.24	3.14	2.33	0.07
23/05/84	59.36	27.52	7.50	3.05	2.31	0.22
20/06/84	61.50	27.44	6.46	2.73	1.64	0.16
18/07/84	62.79	24.90	6.90	3.07	2.10	0.17
Mean	56.55	28.84	8.00	3.66	2.78	0.17
Std.dev.	5.41	4.03	1.08	0.79	0.99	0.05

Table 10.4 Non-ferrous metal proportions within road sediments (%).

From consideration of the Figure and Table it can be seen that lead predominated with a mean value of approximately 56% and a range between 43 and 63%. In order of magnitude this was followed by zinc (mean of 29%), copper (8%), chromium (4%), nickel (3%) and cadmium (0.17%). The zinc and lead proportions that resulted from the deposit cannister samples were lower than the latter values, the mean values of which were 42 and 38% respectively, these were then folowed by copper (11%), nickel (4.5%), chromium (2%) and cadmium (1.47%), therefore displaying a different pattern to those of the road sediment samples. This may suggest variation in the source of metals within the two types of samples, although it should be remembered that part of the deposit cannister proportions will contribute to the road sediment samples.

The proportions within the road sediments were found to remain fairly constant througout the year. Lead proportions, however, were higher during the summer period, but decreased during the winter in favour of zinc, copper, chromium and nickel, which once more was possibly due to the winter salting period. This possibility will be discussed further in Section 10.2.4.

10.2.2 Correlation between Metals

Correlation matrices were computed to study the inter relationships between various pairs of metals within the road sediment samples. The correlation matrices were calculated for all road sediment samples bulked together and for each individual sampling period, an example of which is given in Table 10.5. A correlation matrix was also calculated for the means of the individual sampling periods and is presented in Table 10.6.

METAL	Iron	Lead	Zinc	Copper	Chromium	Nickel	Cadmium
Iron	1.0						
Lead	0.22	1.0					
Zinc	0.42	0.38	1.0				
Copper	0.58	0.08	0.85	1.0			
Chromium	0.45	0.26	0.71	0.67	1.0		
Nickel	0.64	0.29	0.76	0.73	0.70	1.0	
Cadmium	0.50	0.003	0.51	0.52	0.40	0.71	1.0

Table 10.5 Road sediment correlation matrix for 23/08/83.

METAL	Iron	Lead	Zinc	Copper	Chromium	Nickel	Cadmium
Iron	1.0						
Lead	0.57	1.0					
Zinc	0.40	0.57	1.0				
Copper	0.55	0.75	0.49	1.0			
Chromium	0.08	0.53	0.25	0.45	1.0		
Nickel	0.30	0.20	0.02	0.26	0.34	1.0	
Cadmium	0.33	0.73	0.49	0.70	0.26	-0.05	1.0

Table 10.6 Road sediment correlation matrix for the mean data.

The correlation matrix computed for all of the road sediment samples displayed no significant correlations between any two metals. The highest correlation was observed between iron and zinc, with a correlation coefficient (r) equal to 0.55. The correlation matrix for the mean values (Table 10.6) also displayed no significant correlations, however, slight correlations were found between lead and copper (r = 0.75), lead and cadmium (r = 0.73) and copper and cadmium (r = 0.70).

From consideration of the correlation matrices for each individual sampling event different patterns were shown to emerge throughout the year. The significant correlations and the time of occurrence are presented in Table 10.7.

From consideration of the Table it can be seen that the largest number of significant correlations were between lead and copper, lead and zinc, iron and nickel and copper and nickel, the majority of which tended to occur during the winter months. This would suggest a common source of metals, such as road salting, which was at its maximum during this period.

The most significant correlations observed were between lead and zinc and lead and copper (r = 0.91) in February, which was most likely a result of the winter salting period, which peaked in January and February. However, it may also be attributed to vehicles, since a greater amount of pollutants are emitted during cold operating procedures, especially lead (Section 5.3.2.4.2.2).

In conclusion therefore, as with the deposit cannister samples, there was seen to be no consistent significant correlations between any pair of metals within the road sediment samples.

Correlation	Correlation Coefficient (r)	Date
Fe : Pb	0.79, 0.82, 0.80	09/08/83, 23/05/84, 18/07/84
Fe : Zn	0.70	29/02/84
Fe : Cu	0.76	18/07/84
Fe : Ni	0.81, 0.85, 0.81, 0.73	26/09/83, 07/12/83, 28/03/84 23/05/84
Pb : Zn	0.91, 0.82, 0.80, 0.75	01/02/84, 29/02/84, 28/03/84 23/05/84
Pb : Cu	0.91, 0.75, 0.73, 0.80, 0.77	01/02/84, 29/02/84, 23/05/84 20/06/84, 18/07/84
Pb : Ni	0.71, 0.82	25/04/84, 20/06/84
Zn : Cu	0.85, 0.89, 0.80	23/08/83, 01/02/84, 25/04/84
Zn : Cr	0.71	23/08/83
Zn : Ni	0.76, 0.85, 0.71	23/08/83, 01/02/84, 28/03/84
Zn : Cd	0.79	26/09/83
Cu : Ni	0.73, 0.79, 0.78 0.87	23/08/83, 29/02/84, 28/03/84 20/06/84
Cu : Cd	0.83	09/11/83
Cr : Ni	0.70, 0.79	23/08/83, 28/03/84
Ni : Cd	0.71, 0.76	23/08/83, 09/11/83

Table 10.7 Road sediment significant correlation coefficients.

10.2.3 Temporal Variations

The individual metal concentrations for each location during each sampling event were determined and a mean value obtained. The mean values were taken to be representative of the whole catchment and have been previously presented in Table 10.1.

10.2.3.1 Total Metals

The total metal concentrations (Figure 10.3 (a))displayed a seasonal variation. The lowest concentrations occurred during October, with a mean concentration of 15544 mg/kg. Subsequently there was an overall gradual increase with time until a peak was attained during August and September with levels reaching 28835 mg/kg in the latter. An anomaly within this general trend was observed in December when concentrations reached 26872 mg/kg, this could have been a result of the salting event which occurred immediately prior to this date (see Section 10.2.4).

10.2.3.2 Iron

As would be expected from its natural occurrence in the environment, iron follows the pattern of total metals very closely (Figure 10.3 (b)), and has already been noted to be a dominant metal within all samples. The minimum concentrations were found during October, November and March, with values of 14440, 16463 and 15734 mg/kg respectively, and a peak concentration of 27009 mg/kg in September. The peak concentration may have been due to the dust accumulation over the warmer drier months which would allow a larger percentage input of soil to the road sediments.

10.2.3.3 Lead

Lead displayed a slight seasonal trend (Figure 10.3 (c)). Higher levels tended to occur during the summer, with concentrations reaching 1522 mg/kg in June. Lower levels were observed during the winter months, with a minimum of 500 mg/kg in October. This may have been a function of traffic density within the catchment during the period, however, later analyses showed there to be no relationship between traffic density and lead levels throughout the year. Another hypothesis is that the drier periods during the summer encouraged the accumulation of vehicle emitted lead particulates to the road surface, which has been partly substantiated by the observation of a slight negative correlation between total rainfall and the concentration of lead in the road sediments. The latter relationship was also found to exist between the other metals but to a lesser extent.

The seasonal variations in lead levels within the road sediments of Chelmsley Wood contradict those found by Archer and Barratt (1976) for lead in Birmingham dust. Evidence of a seasonal trend was believed to be present but higher levels occurred in winter as opposed to the summer, however, the data was insufficient to confirm the hypothesis.

10.2.3.4 Zinc and Copper

Zinc and copper concentrations remained fairly constant throughout the year (Figures 10.3 (d) and 10.3 (e) respectively), the average values of which were 466 and 132 mg/kg respectively.

Temporal variation

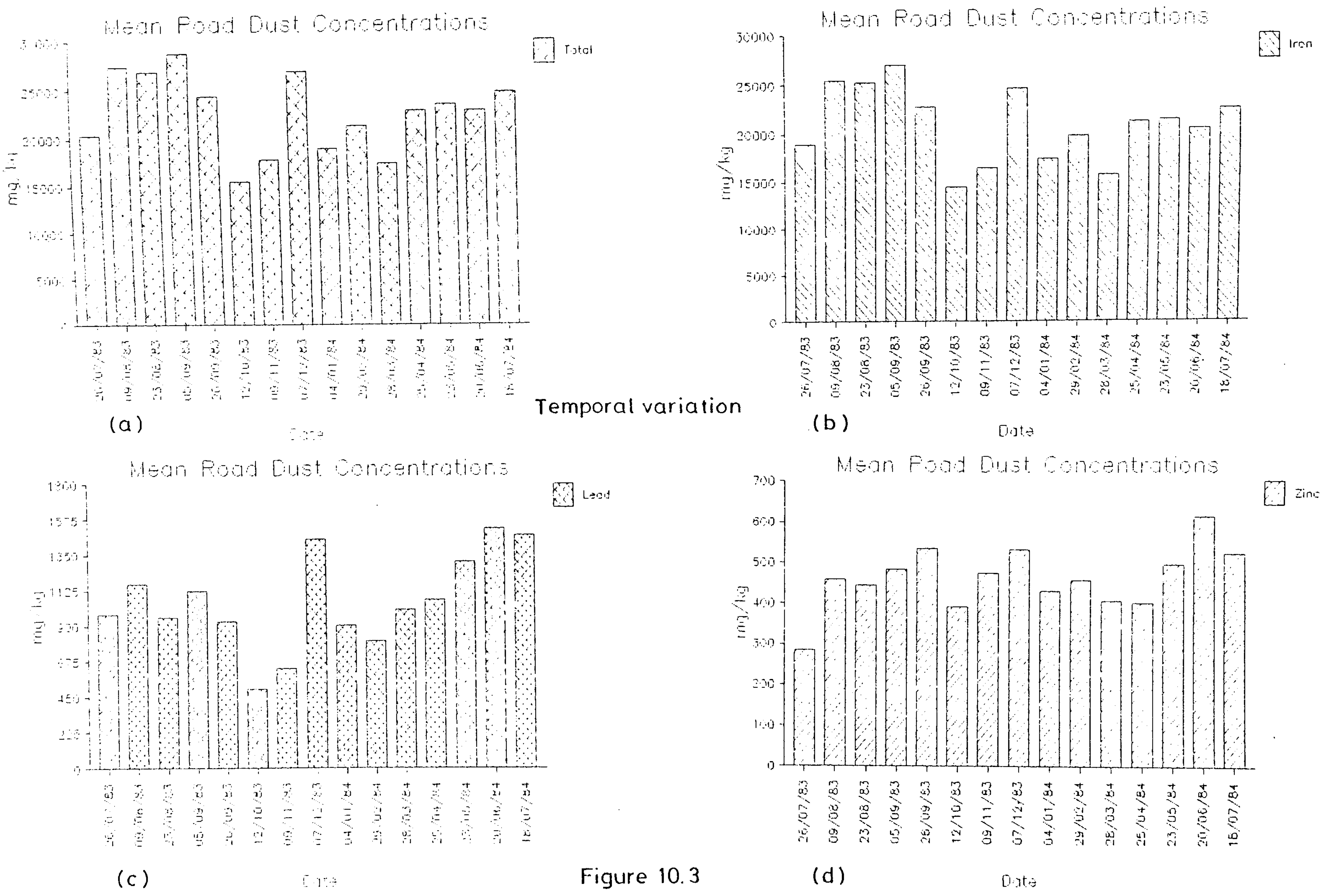


Figure 10.3

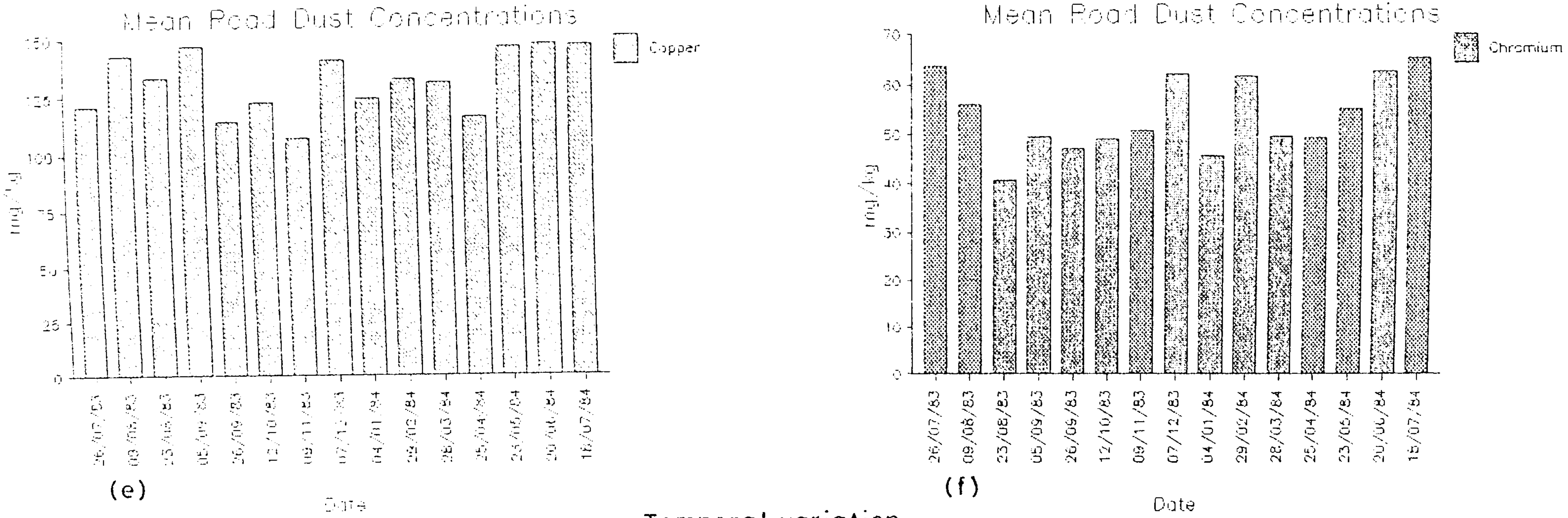
10.2.3.5 Chromium, Nickel and Cadmium

Chromium, nickel and cadmium concentrations tended to fluctuate fairly randomly about a mean value throughout the year (Figures 10.3 (f), 10.3 (g) and 10.3 (h), respectively), with no distinct seasonal pattern. A very high nickel value was observed in August, with a mean of 96 mg/kg. The high mean value was a result of two samples having exceedingly high concentrations reaching 735 mg/kg.

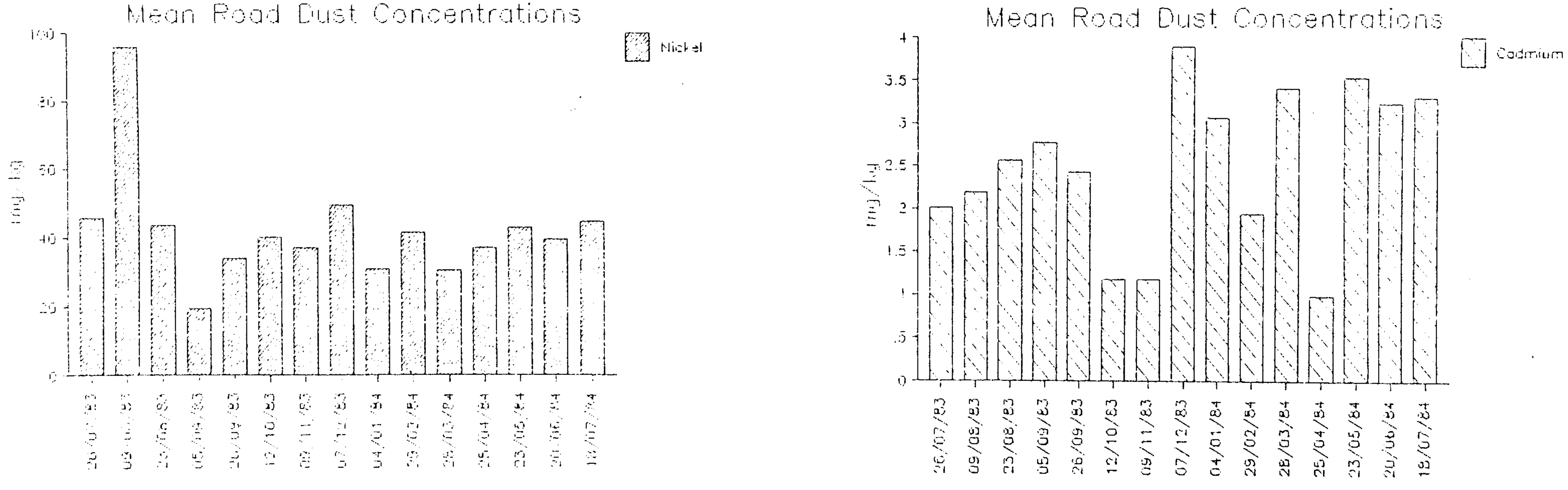
10.2.3.6 Discussion

With the exception of lead and iron, no distinct seasonal patterns within the road sediment metal concentrations could be identified. Lead and iron appeared to exhibit slight seasonal variations with minimum concentrations occurring during the winter months and higher levels during the summer.

No significant correlations were seen between the road sediment metal concentrations and the monthly traffic flow numbers which were probably a consequence of the fact that the data were on such a large scale, i.e. for the whole catchment, that only the small variations were seen within the road sediments. The sources of pollutants were probably localized, such as vehicles leaking oil, abraded vehicular materials or the breakdown of the road surface itself. Further, the data required to calculate the monthly traffic flow figures were not specific to the study area and local seasonal traffic patterns could have existed which were not recorded.



Temporal variation



(g) Date

Figure 10.3 cont

(h) Date

The metal concentrations measured were susceptible to the time of sampling, for example, if the samples were taken immediately after a storm event much of the road sediment would have been removed or redistributed by the water flow (Reinertsen (1981)), and after long dry periods greater accumulation of solids would have occurred, thus giving different metal concentrations.

10.2.4 Comparison with Road Salting and Street Cleaning Records

At the time of peak de-icing activity it would be expected that the concentrations of metals would show an increase (especially those for nickel, lead, zinc and copper), but by visual inspection of the data no such pattern was evident. However, the observation may have been due to the fact that the samples of road sediment were not taken at a time sufficiently close to a salting event to experience any effect from salting. The dates for the road salting events were given in Table 7.3, if these are compared to the dates the road sediments were sampled it can be seen that on three occasions road salting directly preceeded road sediment sampling. The occasions of road salting were 05/12/83, 04/04/84 and 01/02/84 and the road sediment samples were taken on 07/12/83, 04/01/84 and 01/02/84 respectively. The latter would explain the higher metal concentrations during the previous periods, especially the peak concentrations of all metals during December. If the three monthly mean figures were reduced to compensate for road salting, a more seasonal trend would be observed for the majority of metals.

Street cleansing has also been found to effect heavy metal concentrations in road sediments. The dates for the street cleaning events were presented in Table 7.4. From consideration of the Table and the dates when the road sediment samples were taken it is apparent that from February to July all road sediment samples were taken on the day of a street cleaning event, or failing that, the day after, (see Table 10.8).

The metal concentrations varied quite considerably during these periods and as a result any direct comparison was difficult to assess. Observed metal concentrations tended to show little difference from those found during periods when street cleaning was not carried out immediately before a sampling event.

The lack of any significant correlation may have been due to the period of sampling and the method of sample collection. The former may have been to long to detect any changes occurring over shorter periods of time. Many of the sampling events were taken soon after a cleaning event and would therefore be expected to display little variation. In order to quantify such changes it would be necessary to take samples over shorter periods of time, from identical sites within the catchment.

Due to the vast amount of data acquired only the overall averages were employed which would have masked the effects of localized variations. The method of sampling may also have been at fault, since samples were only taken wherever sufficient sediment was found, which was not necessarily in an identical place each time.

Street Cleaning Date	Road Sediment Sampling Date
28/02/84	29/02/84
28/03/84	28/03/84
24/04/84	25/04/84
22/05/84	23/05/84
19/06/84	20/06/84
18/07/84	18/07/84

Table 10.8 Comparison of street cleaning dates to road sediment sampling dates.

In conclusion therefore, if relationships are to be identified between the metal content of the street sediments and road salting/cleaning events, it would be necessary to look at the raw data for specific sites in greater detail and to sample more frequently. Unfortunately the brief of this project did not allow for such studies and it is clear that the data gathered cannot be used for detailed evaluation, but only used to provide an overview of the trends occurring within the catchment.

10.2.5 Comparison with Metal Deposition Rates

When comparing the metal concentrations within the road sediment samples to those of metal deposition rates obtained from the deposit cannisters, no significant correlations were found for the majority of metals. However, higher than average nickel levels found in the road sediments during November and January coincided with higher than average nickel inputs from deposition during these periods. The exceptionally high nickel level for road sediments observed in August was not reflected within the deposit cannister results, and was probably due to other anthropogenic sources direct to the road surface.

Iron showed no consistent correlation, however, higher than average road sediment levels observed during August and September were comparable with higher than average iron levels within the deposit cannister samples during the same period. Similarly, below average iron levels were observed during October and December, and were reflected by low iron levels within the deposition during the period.

The metal levels found within the road sediments did not correlate directly to those found within the deposition, although, as with nickel and iron, similar trends occurred. The metal deposition rates must be reflected within the road sediments at some level. Since deposition only contributes a small fraction of the total input, other sources of metal, such as the soil and traffic, would most likely be greater and thus mask the contribution caused by the atmospheric deposition of metals.

10.2.6 Spatial Variations

In order to determine any significant spatial variation in the metal concentration of the road sediments, the arithmetic mean of the metal concentrations were determined for each location for the entire sampling period. The results are presented in Table 10.9.

The spacial variation of metal concentrations within the road sediments were not homogenous across the catchment, which may have been a result of the variation in number of samples taken at each location throughout the year. Only eleven locations (1, 2, 4, 5, 7, 8, 9, 12, 15, 16 and 21) were sampled consistently throughout the year. However, all of the available information was used for all 24 sampling sites to obtain an overview for the entire catchment.

LOCATION	IRON	LEAD	ZINC	COPPER	CHROMIUM	NICKEL	CADMIUM	TOTAL
1	23536	1327	663	143.23	50.41	44.20	2.49	25769
2	26243	1870	656	172.07	56.15	45.79	2.58	29045
3	23672	569	281	76.20	43.82	25.85	1.42	24670
4	19799	1040	455	131.66	45.76	46.47	1.64	21519
5	22639	1869	494	168.03	50.10	52.92	2.79	25275
6	24323	2251	535	152.80	44.98	125.29	2.42	27432
7	17569	634	347	103.79	37.97	29.58	2.23	18725
8	15008	482	362	73.02	29.10	31.92	3.23	15989
9	19936	1047	293	118.47	34.97	73.74	1.84	21505
10	20504	1098	292	98.79	34.87	30.40	1.51	22059
11	21089	1120	445	117.61	75.12	33.14	1.78	22882
12	18785	1372	679	127.42	71.18	36.25	2.82	21075
13	21875	478	654	602.70	66.97	36.31	1.99	23716
14	26716	306	337	114.05	65.50	55.64	4.13	27598
15	25043	1520	468	142.90	64.32	49.71	2.08	27290
16	21865	360	348	106.22	53.48	42.97	3.87	22780
17	20371	732	459	106.43	44.65	39.79	2.24	21755
18	17612	502	332	79.46	27.96	32.04	1.75	18586
19	21600	610	365	69.25	33.86	33.76	1.40	22713
20	15577	204	211	50.63	22.45	21.96	1.14	16088
21	22486	1122	447	134.76	108.88	36.23	2.34	24337
22	19047	598	365	84.36	148.97	32.58	1.91	20279
23	23569	668	748	87.43	35.52	37.94	3.35	25149
24	17310	758	483	101.19	34.95	35.90	1.89	18724
Mean	21091	939	446	131.74	53.41	42.93	2.28	22707

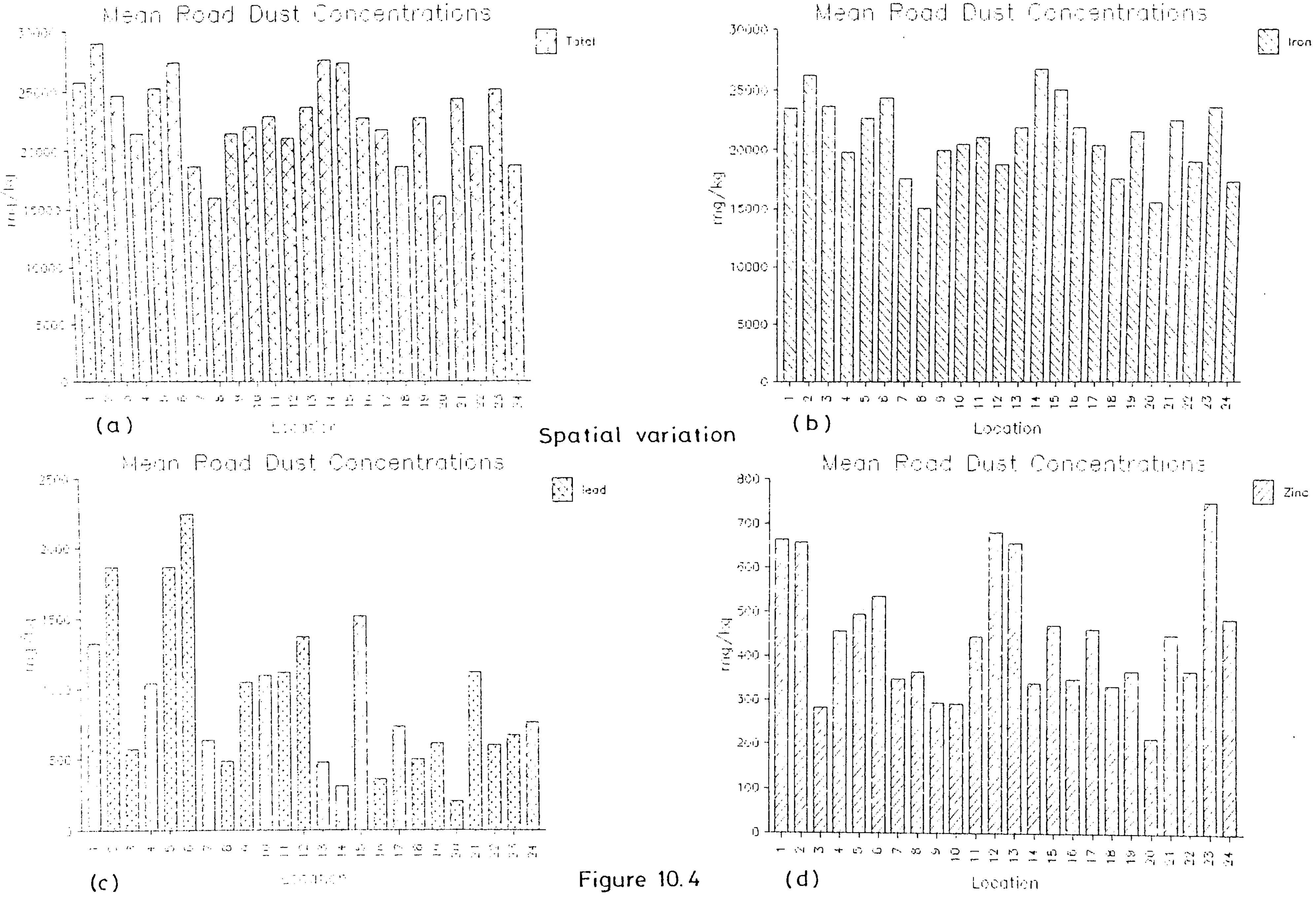
Table 10.9 Spacial Variation of road sediment concentrations (mg/kg).

10.2.6.1 Total Metals

Total metals tended to decrease from the outer perimeter of the catchment towards the centre see Figures 10.4 (a) and 10.5. There were, however, two abnormalities within this general trend, at locations 3 and 14, which were appreciably above the mean value of 22706 mg/kg. Samples from locations 3 and 14 were only taken on a few occasions and hence this may have produced a biased result. Location 14 was a secluded area whilst location 3 was located on a major road.

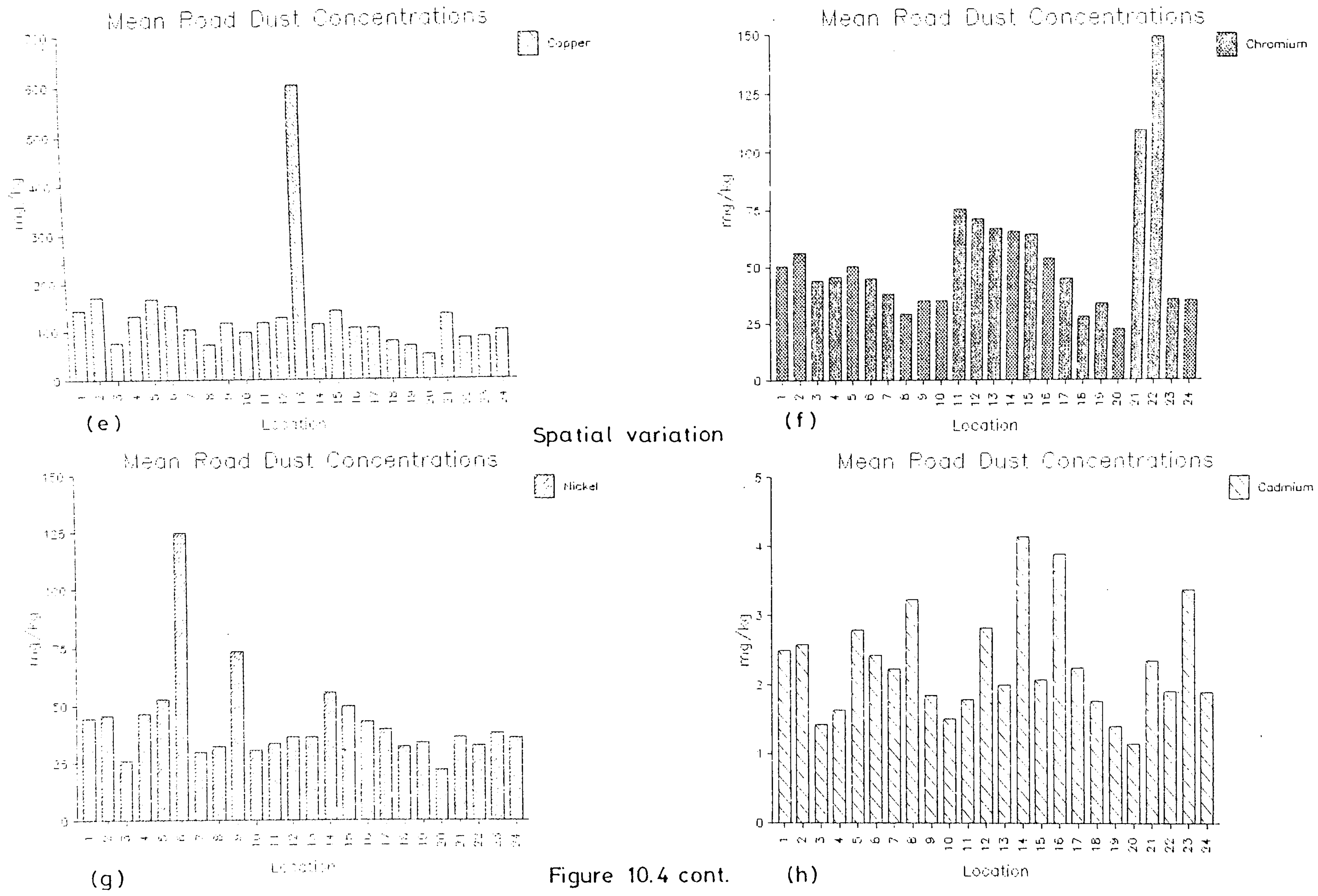
10.2.6.2 Iron

Iron followed a similar spacial pattern to that of the total metals. The mean concentration was 21090 mg/kg with a range from 15000 to 26700 mg/kg. However, there was two spurious results at locations 3 and 14, see Figures 10.4 (b) and 10.6. The maximum recorded level was at location 14, a very secluded area with parked and abandoned vehicles a common feature. It is possible that the vehicles could have been a source of metals to the road sediments, especially iron as a result of the deterioration of the vehicle body work. The predominantly high levels around the east of the catchment were probably due to the effects of increased traffic flows and the effects of the motorway, the feeder road and the agricultural lands surrounding the area. Location 3 also experienced higher than average iron levels, which may have been a result of the sampling point being located on a major road.



Spatial variation

Figure 10.4



(e) (f)

Spatial variation

(g) (h)

Figure 10.4 cont.

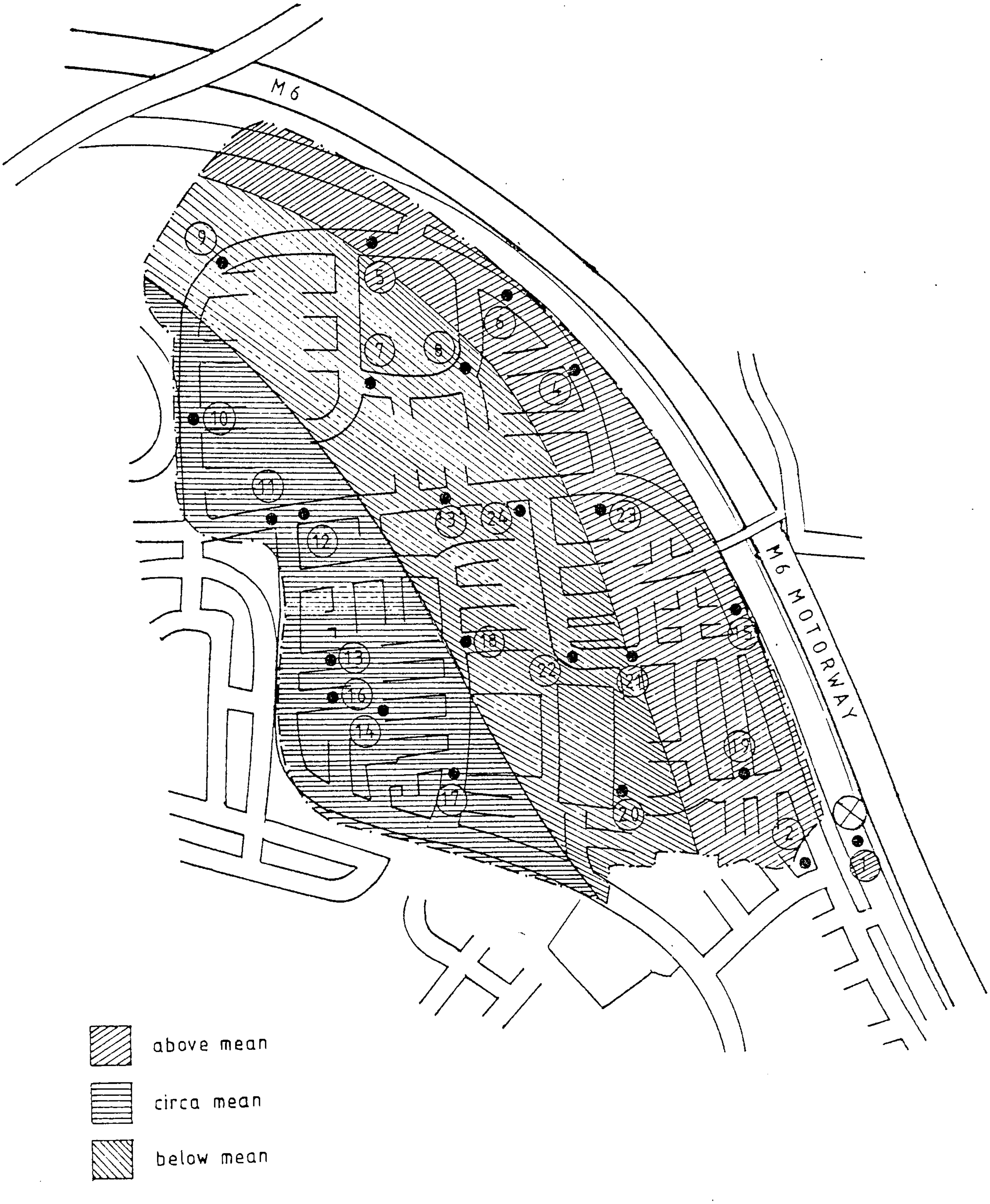


Figure 10.5 Spatial variation of total metals concentration in road sediments.

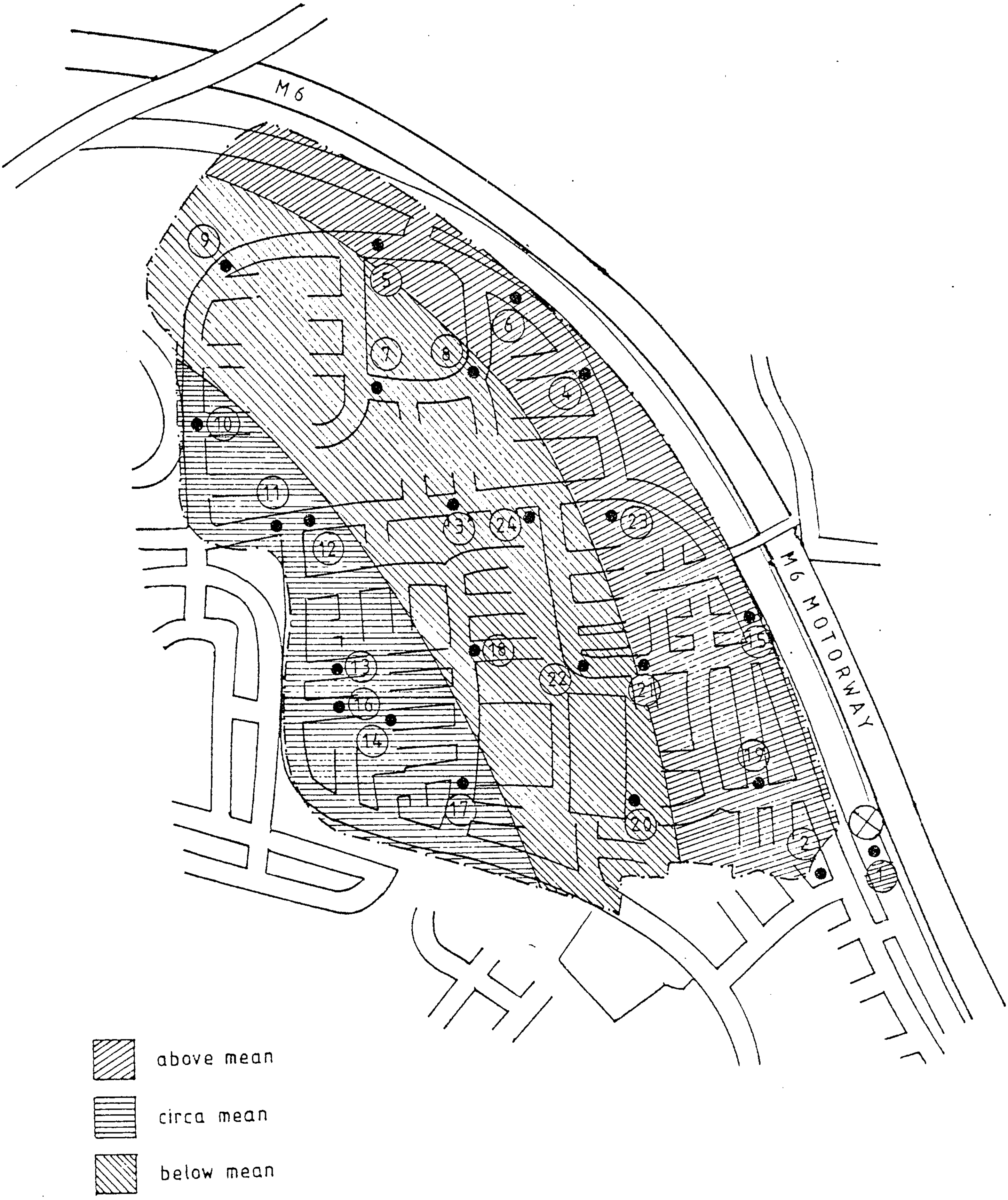


Figure 10.6 Spatial variation of iron concentrations in road sediments.

10.2.6.3 Lead

The lead concentrations across the catchment displayed considerable variation (see Figures 10.4 (c) and 10.7). The values ranged between 204 and 22501 mg/kg and had a mean of 939 mg/kg.

Lead is derived from anti-knock compounds in petrol and is introduced into the environment via vehicle exhausts, therefore vehicles are a major source of lead pollution to road dusts (Farmer and Lyon (1977)). The variation in levels found in this study substantiate the previous statement. Higher than average lead concentrations were found to occur along major roads i.e. at locations 1, 2, 5, 6, 11, 12 and 15. Locations 1, 2, 5, 6 and 15 were along the main outer road of the catchment area and were also the nearest to the feeder road and motorway. Locations 11 and 12 were located in the main entry and exit corridor to the area. Lower than average lead levels were found within the interior of the catchment, which was not only protected from any influence from the motorway by residential buildings, but was bounded by less trafficked minor roads. Location 21 experienced a high lead concentration even though it was located on a minor road. This could be attributed to the presence of fragmented yellow paint, from parking restriction lines (lead chromate), which was found to occur within the samples on numerous occasions.

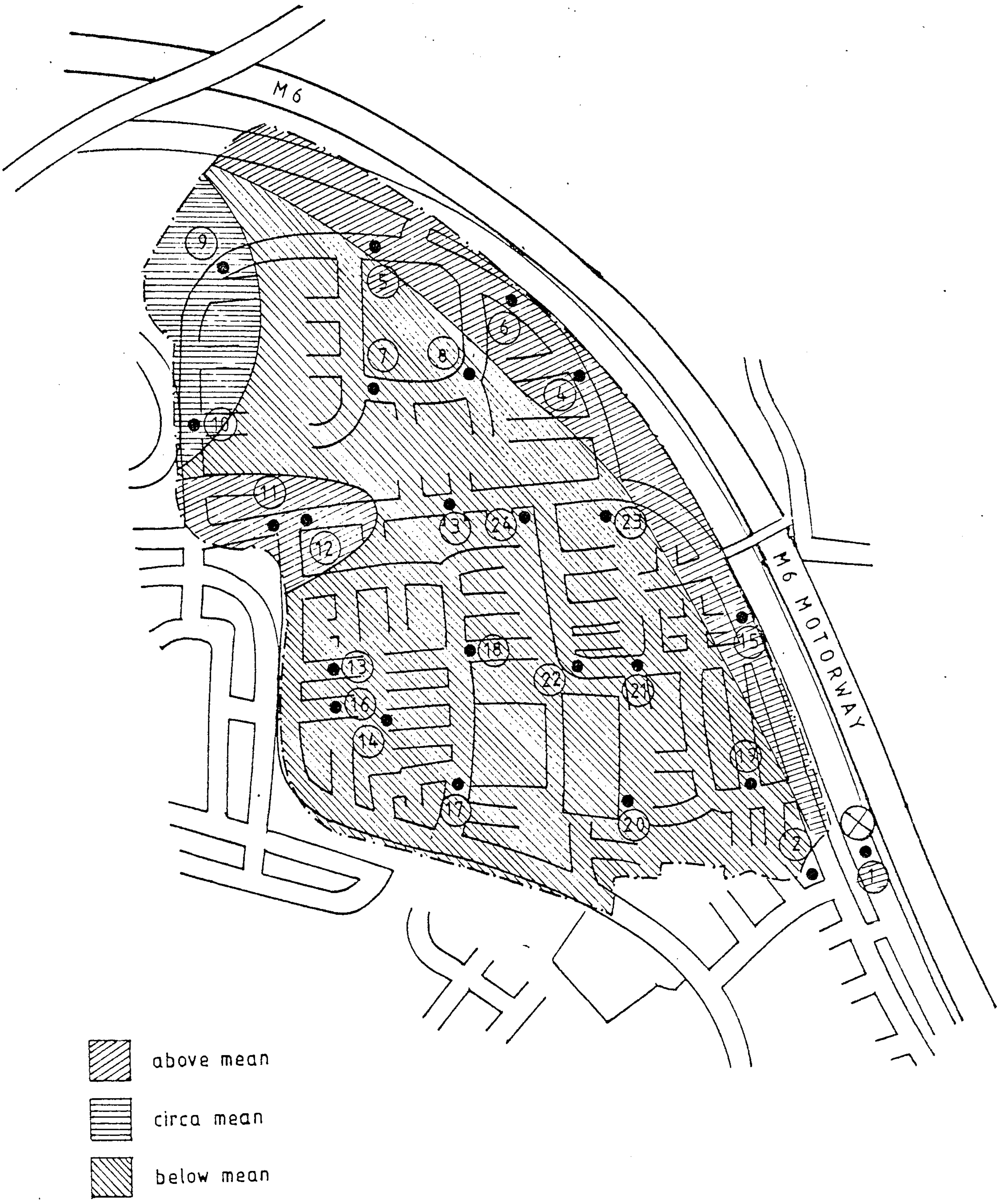


Figure 10.7 Spatial variation of lead concentrations in road sediments.

10.2.6.4 Zinc

Zinc concentrations also displayed spacial variation across the catchment, but less markedly than that for lead (Figures 10.4 (d) and 10.8). The mean value was 446 mg/kg and ranged from 211 to 748 mg/kg.

It would seem probable that zinc concentrations would also vary according to traffic density due to the presence of zinc in vehicle tyres. A slight trend was observed, with higher than average levels occurring along the major road (i.e. locations 1, 2 and 6), and in the main entry and exit corridor to the catchment (see Figure 10.8). There were a couple of high spurious results at locations 23 and 13. The maximum zinc concentrations were found at location 23, where samples were taken on the footpath, which was never swept. As with location 14, location 13 was also sheltered in a cul de sac with parked vehicles a common feature. There always appeared to be much sediment on the road in this location suggesting that the area was only seldom swept.

Lower than average zinc concentrations tended to occur within the centre of the catchment which was protected from outside influences.

As there were abnormalities in the spatial variation of zinc levels it would suggest that there was another source of zinc other than that from vehicles, which could account for the local variations. Such sources may have included soil, litter, vegetation and agricultural practices.

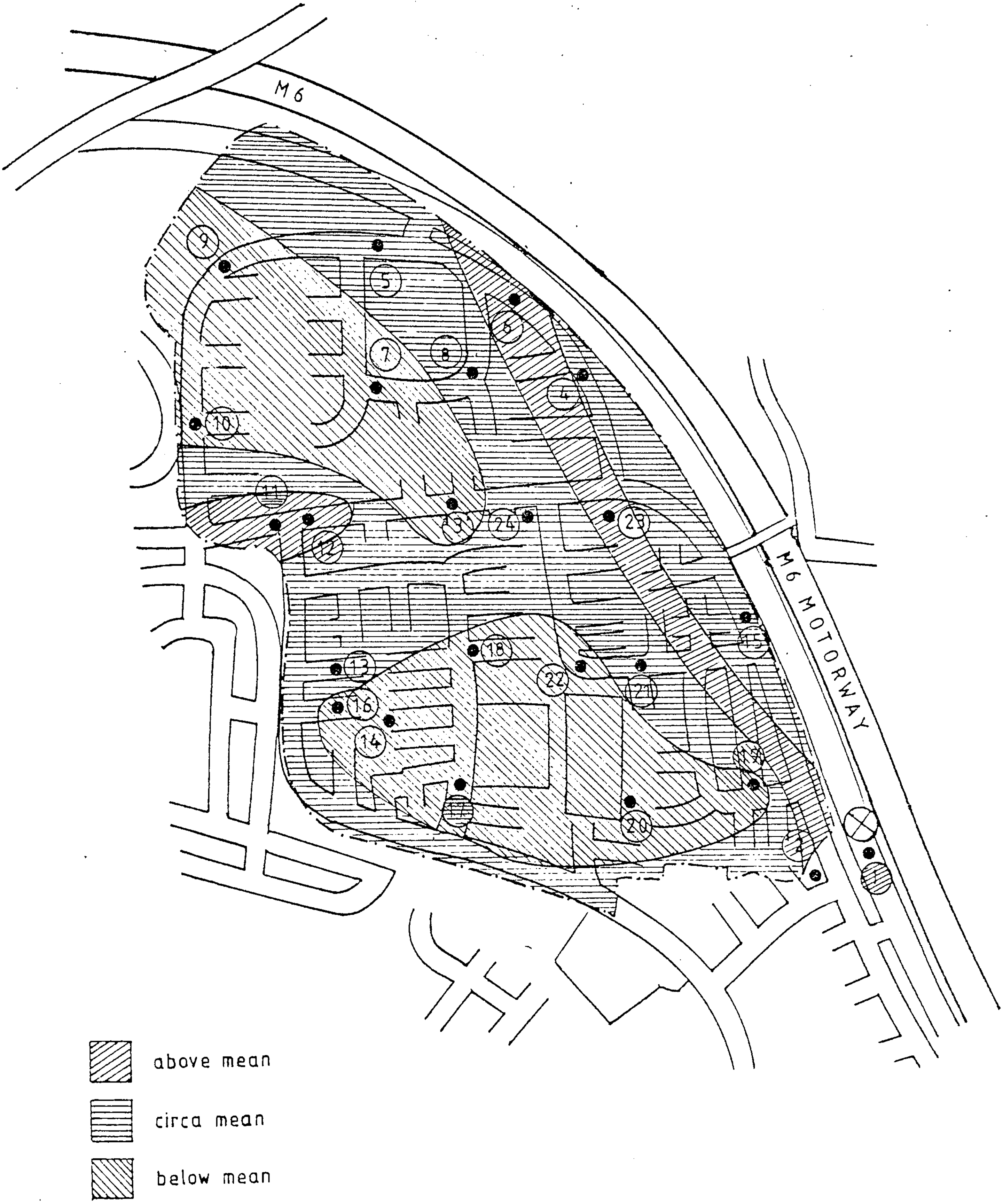


Figure 10.8 Spatial variation of zinc concentrations in road sediments.

10.2.6.5 Copper

Copper concentrations were fairly constant across the catchment, apart from one abnormally high value of approximately 600 mg/kg at location 13 (Figures 10.4 (e) and 10.9). This high mean value was due to an extremely high concentration within tha sample collected on 23/08/83 of 1295 mg/kg. The reason for this is unknown but it was probably due to some local contamination within the area.

The few locations which were found to have copper concentrations greater than the mean value were at locations 2, 5, 6, 15 and 21, the majority of which were located on the main perimeter road (Figure 10.9). Hence there may also be a link between copper concentrations and traffic density. Location 13 again experienced abnormally high concentrations, the reasons for this have been previously discussed for zinc.

10.2.6.6 Chromium

Chromium concentrations displayed a different pattern to those previously mentioned for the other metals (Figures 10.4 (f) and 10.10). Higher than average chromium levels were experienced in a band through the catchment area, with maximum concentrations occurring at locations 21 and 22, with values of 109 and 149 mg/kg respectively. The locations were where fragments of yellow paint, from road surface markings, were often found, and may therefore be a source of chromium. No direct relationship was found between the major roads and the chromium concentration. Below average concentrations (53 mg/kg) were found over the majority of the catchment, with near average values occurring along the boundary road i.e. at locations 1, 2, 4 and 5.

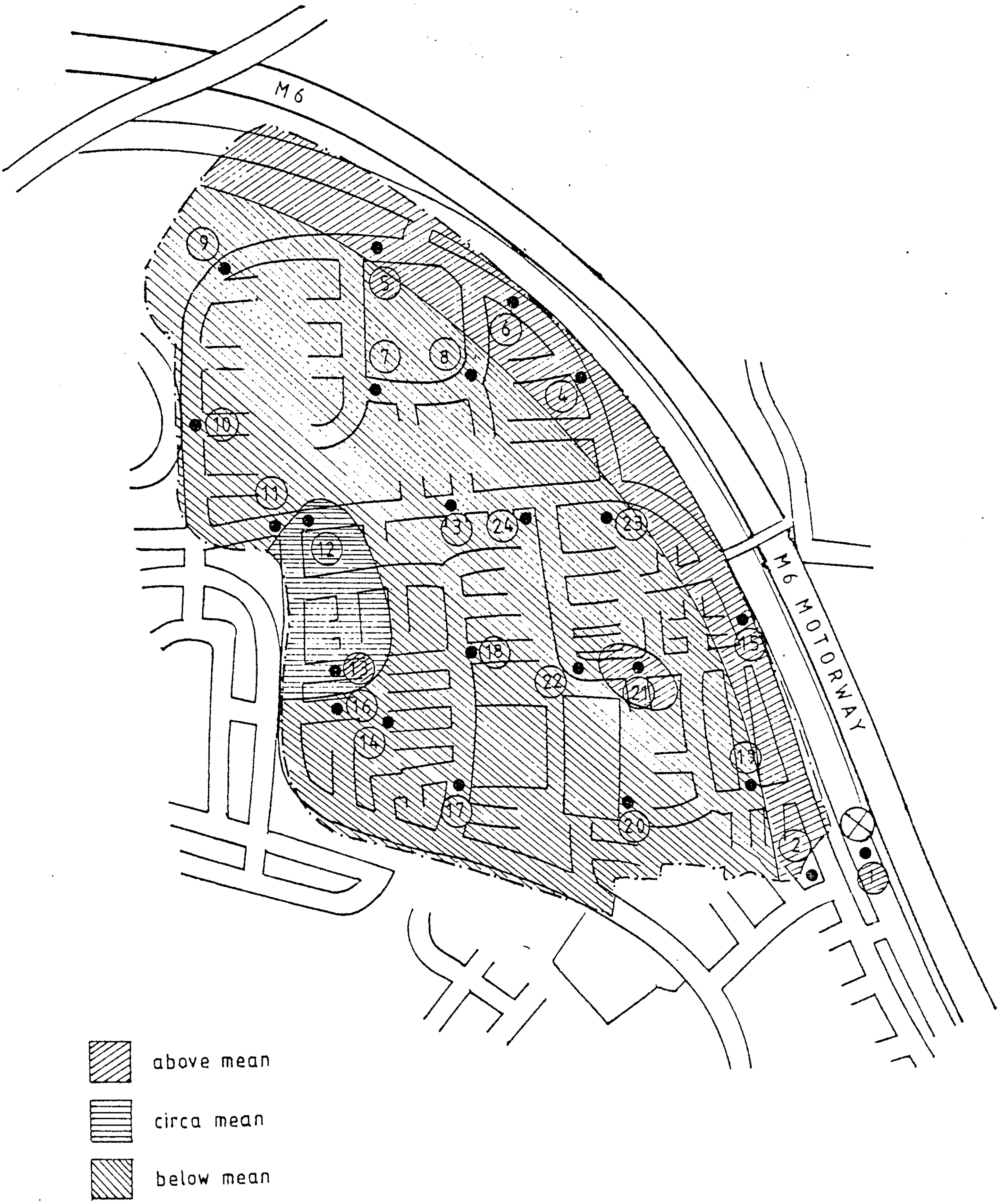


Figure 10.9 Spatial variation of copper concentrations in road sediments.

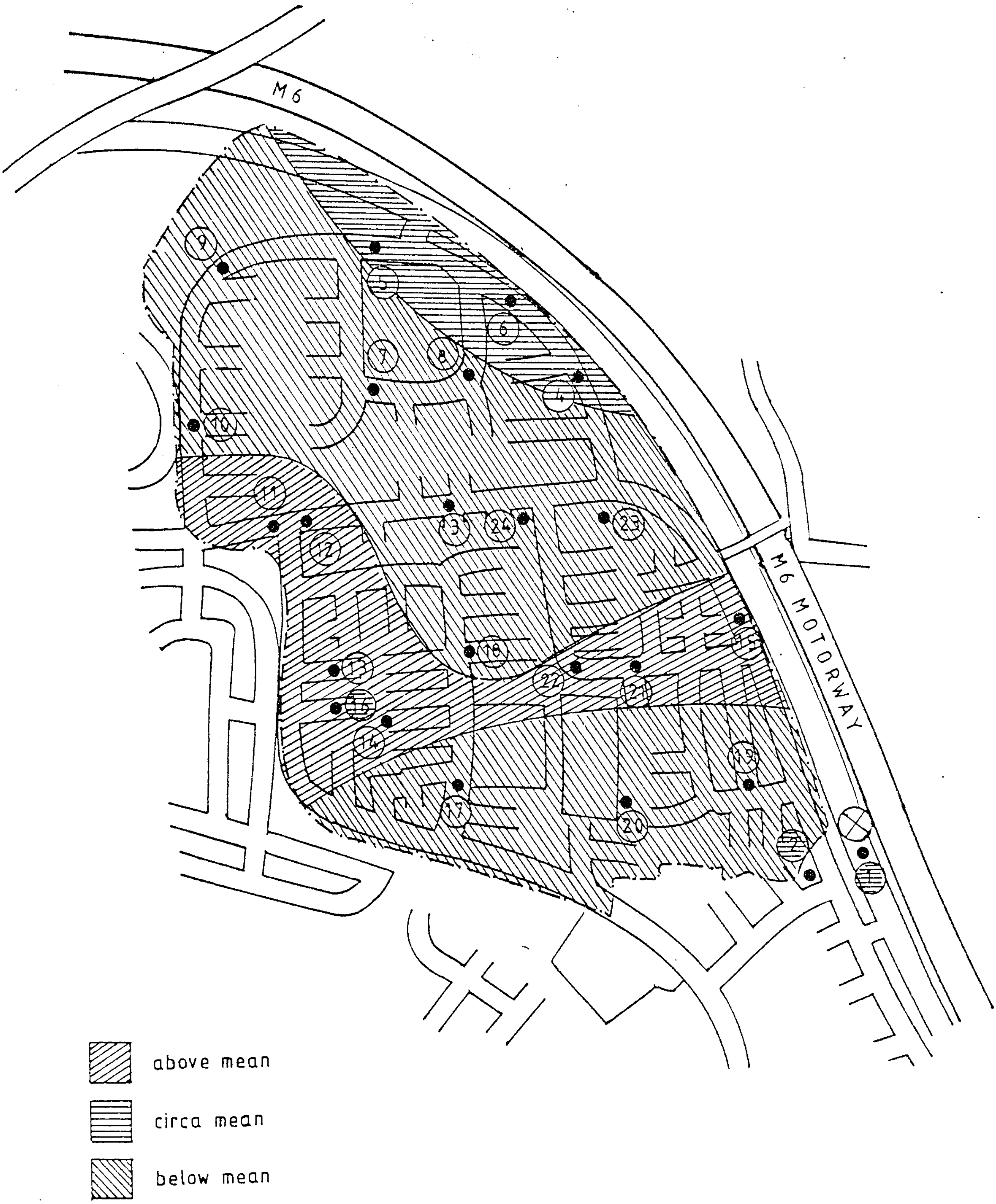


Figure 10.10 Spatial variation of chromium concentrations in road sediments.

10.2.6.7 Nickel

Nickel concentrations tended to fluctuate rather randomly about a mean of 43 mg/kg over the catchment (Figures 10.4 (g) and 10.11). However, one very high level of 125 mg/kg was found at location 6 and this was due to an extremely high nickel concentration within the sample on 09/08/83, of 672 mg/kg, which was probably due to some local contamination within the area. If this value was disregarded the mean nickel level falls to 39 mg/kg. From Figure 10.11 it can be seen that the higher than average levels tended to occur in the northern most section of the area, which would indicate a source from outside the area, possibly from the industries to the north or from the prevailing wind patterns.

Lower than average nickel levels were seen within the interior of the catchment, with a minimum concentration occurring at location 20 with a value of approximately 22 mg/kg. Location 14 once again had a high concentration and the possible reasons for this were discussed for iron.

10.2.6.8 Cadmium

The cadmium concentrations within the road sediment samples showed rather erratic variations across the catchment (Figures 10.4 (h) and 10.12), with no distinct pattern. The maximum levels recorded were at location 14 with a mean concentration of 4.13 mg/kg. The minimum cadmium concentrations were observed at location 20 with a mean value of 1.14 mg/kg. The patterns displayed did not appear to be traffic related as would probably be expected.

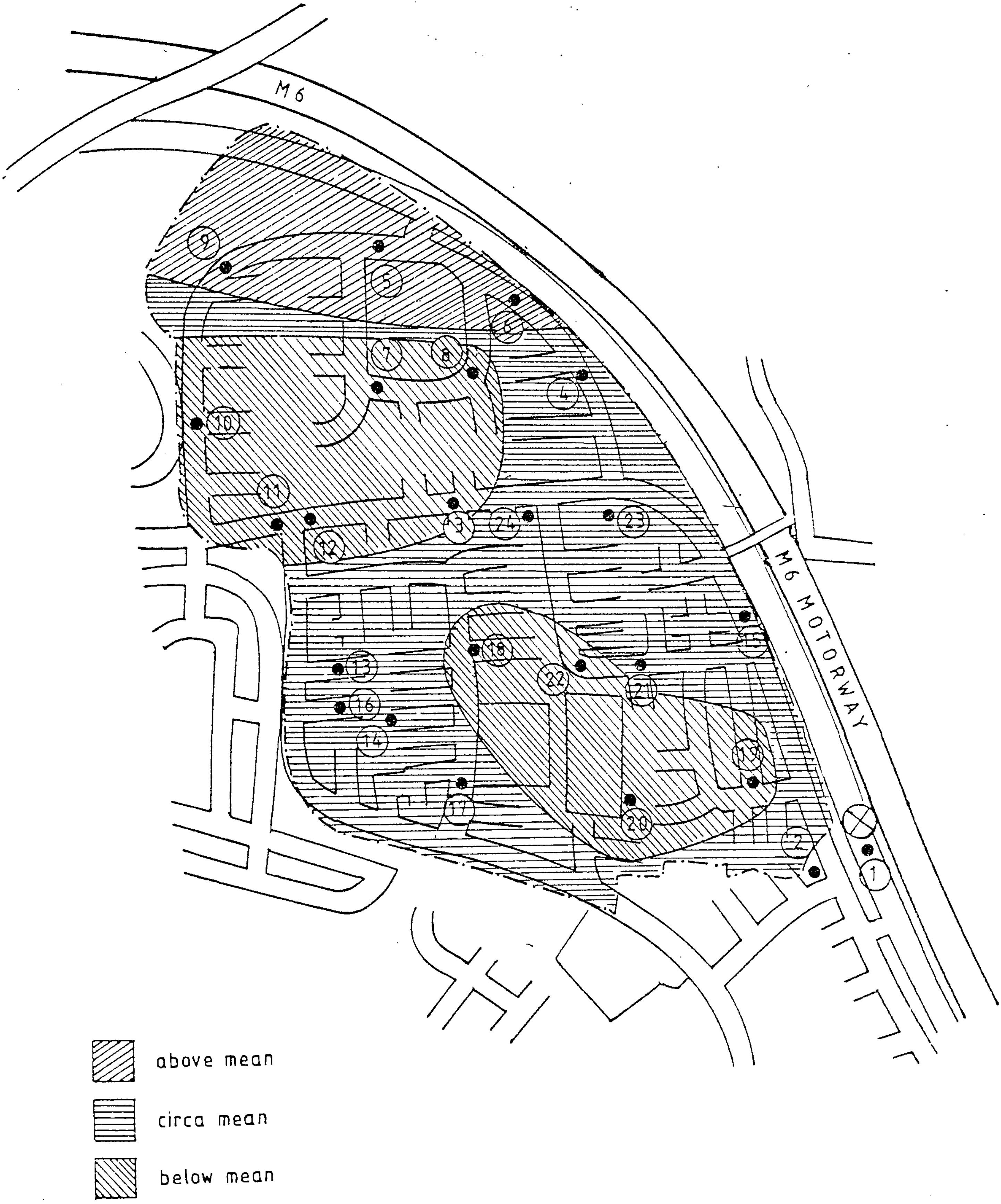


Figure 10.11 Spatial variation of nickel concentrations in road sediments.

Figure 10.12 Spatial variation of cadmium concentrations in road sediments.

However, the cadmium concentrations observed may have been related to vehicles, since many locations which experienced high cadmium levels, often had vehicles in a state of repair e.g. locations 8, 14 and 16. The sample taken at location 23 was taken on a pathway and these samples will be discussed later.

10.2.6.9 Discussion

Some of the metal concentrations were found to be high adjacent to the main entry and exit point to the catchment and along the motorway and feeder road boundary. Lower levels were often found to occur within the more secluded and quiet residential areas.

A number of metals were seen to be elevated along the more heavily trafficked roads i.e. locations 1, 2, 5, 6, 9, 10, 11, 12 and 15. Tables 10.10 and 10.11 give the mean metal concentration of the road sediments on major and minor roads within the catchment.

From consideration of the Tables it can be seen that the mean lead concentrations for locations along the major roads were markedly higher than those on the minor roads i.e. 1371 mg/kg compared with 548 mg/kg respectively. Duggan and Williams (1977) also found that there was a clear reduction in lead concentrations within road dust samples as the density of traffic was reduced.

Lead was the only metal in the study to display a marked increase with increasing traffic density and road usage. However, zinc and iron concentrations were also found to be higher on the busier roads when compared with the minor roads, with levels of 478 and 384 mg/kg and 22324 and 19975 mg/kg respectively.

LOCATION	IRON	LEAD	ZINC	COPPER	CHROMIUM	NICKEL	CADMIUM	TOTAL
1	23536	1327	663	143.23	50.41	44.20	2.49	25767
2	26243	1870	656	172.07	56.15	45.79	2.50	29045
3	23672	569	281	76.20	43.82	25.85	1.42	24670
4	19799	1040	455	131.66	45.76	46.47	1.64	21520
5	22639	1869	494	168.03	50.10	52.92	2.79	25275
6	24321	2251	535	152.80	44.98	125.29	2.42	27432
9	19936	1047	293	118.47	34.97	73.74	1.84	21505
10	20504	1098	292	98.79	34.87	30.40	1.51	22059
11	21089	1120	445	117.61	75.12	32.14	1.79	22882
12	18785	1372	679	127.42	71.18	36.25	2.82	21073
15	25043	1520	468	142.09	64.32	49.71	2.08	27290
Mean	22324	1371	478	131.70	52.00	51.25	2.12	24411
Std.dev.	2441	478	148	28.62	13.50	27.80	0.50	2781

Table 10.10 Metal concentrations on major roads (mg/kg).

LOCATION	IRON	LEAD	ZINC	COPPER	CHROMIUM	NICKEL	CADMIUM	TOTAL
7	17569	634	348	103.80	37.97	29.58	2.23	18725
8	15008	482	362	73.02	29.10	31.92	3.23	15989
13	21875	478	654	602.70	66.97	36.31	1.99	23715
14	26716	306	337	114.05	65.50	55.64	4.13	27598
16	21865	360	348	106.22	53.48	42.97	3.87	22780
17	20371	732	459	106.43	44.65	39.79	2.24	21755
18	17612	502	332	79.46	27.96	32.04	1.75	18586
19	21600	610	365	69.25	33.86	33.76	1.39	22713
20	15577	204	211	50.63	22.45	21.96	1.14	16088
21	22486	1122	447	134.76	108.88	36.23	2.34	24337
22	19047	598	365	84.36	148.97	32.58	1.91	20279
Mean	19975	548	384	136.60	58.16	35.71	2.38	21142
Std.dev.	3435	245	110	155.70	38.97	8.06	0.97	3595

Table 10.11 Metal concentrations on minor roads (mg/kg).

Mean copper concentrations within the road sediments were only slightly higher along the major roads than the minor roads. However, if the higher value at location 13 is disregarded, the mean for the minor roads now falls from 138 to 92 mg/kg, indicating that traffic density may well be a cause of the elevated concentrations in certain locations.

High levels of chromium, and to a lesser extent lead, were found at locations 21 and 22, both sampling points of which were on a quiet minor road. The reason for such elevated levels may have been due to the fragments of yellow paint, from parking restriction lines, which were often found in these samples. The paint (containing lead chromate) has been postulated as a possible source of both lead and chromium within road surface sediments (Turner (1971)), but there are conflicting views regarding this (Harrison (1979)), see Section 4.2. The fact that flakes of such paint were observed within the samples does suggest a possible source of such metals within the road sediment samples taken in Chelmsley Wood.

Location 20 experienced the minimum concentrations of all metals analysed, with the exception of iron. This was a rather sheltered location at the end of a cul de sac, and all samples contained large quantities of sand. The presence of this material may have effectively reduced the concentrations of the other metals per unit weight.

The average concentrations of metals on salted and unsalted roads were also calculated and were shown to coincide for values obtained from the major and minor roads. All major roads within the area were salted since these were the priority routes, whereas the minor roads were not salted. It is therefore difficult to deduce whether the higher concentrations of metals on the major roads were specifically due to the higher traffic densities or due to a contributory source such as road salt. However, as road salting does not occur throughout the year, it would seem likely that traffic density would be the major source with road salt an additional source during the winter months.

Two pavement sediment samples were also taken, at locations 23 and 24. The average metal concentrations at these locations are given in Table 10.12.

Harrop (1984) found that sediments from path surfaces had lower metal concentrations than those of road surface sediments. Conversely, Reinertsen (1981) concluded that the concentrations of metals, calculated as mg/m^2, were often higher on the pavement than the roadway and therefore the contribution from the pavement to the surface runoff was important despite its small dimensions.

The metal concentrations observed at Chelmsley Wood, with the notable exception of zinc, fell within the ranges obtained for the minor roads. Zinc levels were unexpectedly high and were comparable to levels found on busy roads (615 mg/kg compared with 498 mg/kg respectively). The increased concentration levels add weight to the hypothesis that there is in fact an additional source of zinc within the catchment, which is not vehicle related. It may be assumed to be from either the soil or from aerial deposition.

LOCATION	IRON	LEAD	ZINC	COPPER	CHROMIUM	NICKEL	CADMIUM	TOTAL
23	23569	668	748	87.43	35.52	37.94	3.35	25149
24	17310	758	483	101.19	34.95	35.90	1.89	18724
Mean	20439	713	615	94.31	35.24	36.92	2.62	21937
Std.dev.	4426	63	187	9.73	0.40	1.44	1.04	4543

Table 10.12 Pavement heavy metal concentrations in Chelmsley Wood. (mg/kg)

CHAPTER 11

SOIL HEAVY METAL CONTENT

11.1 Introduction

Heavy metals are widely distributed in the environment and are present in all uncontaminated soils as a result of the weathering of parent material. This has been evidenced by numerous authors and a summary has been given by Ure and Berrow (1982). In recent years there has been increasing recognition that naturally occurring levels in soil can be elevated, often to toxic proportions, through anthropogenic inputs. The principal sources of heavy metal contamination in the environment are reasonably well recognized and have widely been documented (Davies (1980), Thornton (1980) and Greenland and Hayes (1980)).

Possible sources of heavy metal contamination to soil have been reviewed by Lagerwerff and Specht (1970). The sources included heavy metal impurities present in certain agricultural chemicals, routinely applied to soils and crops which also, due to aerial presence reach the soil and plant cover via precipitation, the use of metal containing pesticides to protect roadside grasses and trees, the presence of local industries which discharge heavy metals into the atmosphere in the form of flumes or dust, the application of de-icing salt and finally motor vehicles.

Motor vehicles provide an important source for a variety of heavy metal pollutants to the environment. Lead is derived mainly from the combustion of leaded petrol and nickel is a result of nickeled gasoline and atmospheric abrasion of nickel containing vehicle parts. Zinc and cadmium are from oils and tyres (Korkish and Hazan (1965) and Specht et al (1965)), the cadmium content of tyres has been quoted to range between 20 to 90 ppm (Lagerwerff and Specht (1970)). Cadmium is also an impurity in some of the common zinc containing additives and cadmium and zinc are often found together in the same source materials and are chemical kin.

The presence of these elements in soils and vegetation along roads and motorways is probably a result of mechanical wear and tear. The metals are deposited as a fine dust on the roadway which are subsequently transmitted to soils and vegetation (Ward et al (1977)).

There is a wealth of evidence (e.g. Chow and Johnson (1965) and Le Riche (1968)) which have demonstrated a clear relationship between heavy metal soil pollution and particular urban sources, such as industrial activity, general urban land use and high traffic flows.

When heavy metals enter the environment through natural weathering processes and anthropogenic emissions, normal biogeochemical cycles are followed such as transportation by air, water and gravity, until they reach a geochemical sink. Soil is an important sink and heavy metals have been shown to accumulate rapidly, but are only depleted very slowly. Therefore land, especially in industrial areas, represents a major reservoir of heavy metals and forms an important link through which heavy metals may be transferred to man.

11.2 'Normal' Heavy Metal Levels in Soils

In order to interpret the results of the total metal concentrations found within the soil samples, it was necessary to make a comparison with 'expected' or 'normal' levels of metals found in unpolluted soils.

A large scale survey to establish 'normal' levels of heavy metals in agricultural (unpolluted) soils was undertaken by ADAS (Agricultural Development and Advisory Service) of the Ministry of Agriculture, Fisheries and Food, and was reported by Archer (1980). Soil samples from 16 farms in each of the 12 ADAS regions (in England and Wales) were taken for analysis. The details of the resulting rural baseline are summarized in Table 11.1.

The study showed that for agricultural soils the amounts of total and extractable lead and zinc were wide ranging. The survey also demonstrated that the heavy metal content of agricultural soils was not consistently related to parent material.

A summary of data for 'normal' levels of heavy metals reported in the literature for uncontaminated soils and for naturally occurring levels from agricultural land was given by Haines (1982) and are presented in Table 11.2. Table 11.3, also taken from Haines (1982), gives the guidelines on contaminated soils and presents the suggested range of values. Both Tables will be used to interpret the results obtained in this study.

	ELEMENT	MEDIAN	RANGE
TOTAL (mg/kg)	Cd	1	0.08 - 10
	Cu	17	1.80 - 195
	Ni	26	4.40 - 228
	Pb	42	5.00 - 1200
	Zn	77	5.00 - 816
EXTRACTABLES (mg/l)	Cu	4.4	0.50 - 74.0
	Ni	1.0	0.12 22.7
	Zn	6.6	0.40 - 97.6

Table 11.1 Median trace element content of soils in England and Wales. (Adapted from Archer (1980))

ELEMENT	Total Heavy Metals mg/kg	
	RANGE	COMMON LEVEL
Pb	2 - 200	10
Zn	10 - 300	30
Cu	2 - 100	20
Cr	5 - 3000	100
Ni	4 - 200	20
Cd	0.1 - 2	10

Table 11.2 Normal (unpolluted) range and common levels of metals in soils. (Adapted from Haines (1982))

ELEMENT	Typical Value	Slight Contamination	Heavy Contamination
Cd	0 - 1	1 - 3	10 - 50
Cu	0 - 100	100 - 200	500 - 2500
Pb	0 - 200	200 - 500	1000 - 5000
Ni	0 - 20	20 - 50	200 - 1000
Zn	0 - 250	250 - 500	1000 - 5000

Table 11.3 Guidelines on contaminated soils (mg/kg). (Adapted from Haines (1982))

11.3 Surveys of Heavy Metals in Urban Soils

Several investigations e.g. Davies (1980), Beavington (1973) and Haines (1982)) have established that heavy metal levels in urban soils may be elevated and present environmental health problems. In fact, Davies (1980) has stressed the point that soil sampling is the ideal method of determining the broad levels of heavy metals in the environment. The study provided substantial evidence to the effect that the heavy metal content of soils in urban areas may show elevation above those considered to naturally occur.

Klein (1972) studied the mean concentrations of heavy metals in four land use types and the results are presented in Table 11.4. The Table demonstrates that levels of heavy metals in soil samples taken from within industrial areas were higher than other land use categories. Beavington (1973) has also shown that the levels of heavy metals in urban soils vary according to the land use.

Many of the studies concluded that contamination of the soil was attributable to industrial point sources and vehicle exhaust emissions. For example, Lagerwerff and Specht (1970) looked at the concentrations of cadmium, nickel, lead and zinc in roadside soil and grass samples. All were found to decrease with distance from the road, indicating a relation with vehicular activity, additionally a decrease in metal concentration with depth in the soil profile was found.

LAND USE	METAL (ppm)			
	Cd	Cu	Pb	Zn
Residential	0.41	8.0	17.9	21.1
Agricultural	0.57	8.8	15.4	22.1
Industrial	0.66	10.3	47.7	56.6
Airport	0.77	10.4	17.9	36.6

Table 11.4 Mean heavy metal concentrations in four land use types. (Klein (1972))

The metal contamination was shown to be related to the composition of gasoline, motor oil and car tyres, and to the roadside deposition of the residues of these materials. It was also found that in spite of the dependence on traffic of roadside cadmium, nickel, lead and zinc, it appeared that high concentrations of one metal in the soil did not necessarily entail high concentrations of another.

Farmer and Lyon (1977) also concluded that automobile lead contributed significantly to lead concentrations in soils adjacent to roads in Glasgow. Also supported was the concept of a rapid fall off in concentration with distance from the road forwarded by Lagerwerff and Specht (1970). A decrease in lead concentration was observed from 500 ppm, 2 m from a busy city intersection, to 145 ppm at a distance of 20 m.

Ward et al (1977) studied cadmium, chromium, copper, lead, nickel and zinc concentrations in soils and pastures along a major motorway in New Zealand. Enhanced levels of all metals were found to be correlated with traffic density. The concentrations also decreased with depth, sugesting the source of aerial deposition was from motor vehicles.

Studies have therefore demonstrated that there is a wide range of factors which contribute to the levels of heavy metals in soils and urban soils in particular. Factors include the nature of the parent rock, climatic influences, human activity (in particular industrial activity), urban development and motor vehicles.

Work by Thornton (1975) and Archer (1980) clearly illustrated that even in 'unpolluted' rural environments, heavy metals in soils displayed wide variation. Soil samples taken from within urban areas also have a wide range of heavy metal levels, from 'normal' (unpolluted) levels to significantly high levels showing marked contamination (Beavington (1973) and Davies (1980)).

11.4 Soil Heavy Metal Content in Chelmsley Wood

The soil sampling programme was designed to yield information on the distribution of total heavy metal levels at various localities throughout the catchment. The object of the sampling programme was to assess the contribution of the soil to the eventual metal concentration in the stormwater runoff.

Two sets of soil samples were taken at ten locations throughout the catchment (see Figure 8.4) for the dates of 01/08/83 and 05/10/83. A description of the locations is given in Table 11.5.

Both topsoil and subsoil samples were taken for analysis at each sampling point. Topsoil samples were taken by removing the top 50 mm of soil with a trowel, subsoil samples were obtained using a plastic coated metal auger (Section 8.4). A number of samples were obtained at each location which were then bulked together to form one sample. The samples were subsequently oven dried, ground and digested in aqua regia acid to obtain the total heavy metal content.

A summary of the mean metal concentration and ranges are presented in Table 11.6.

LOCATION	DESCRIPTION
A	11 Chaffinch Drive - front garden
B	1 Corncrake Drive - front garden
C	Burtons Farm School - shrubbery
D	63 Kingfisher Drive - front garden
E	Bosworth Wood School - shrubbery
F	452 Windward Way - shrubbery (old peoples home)
G	Dove Way car park - shrubbery
H	Tamar Drive - shrubbery
I	Lanchester Way - verge
J	Lanchester Way - woods

Table 11.5 Description of soil sampling sites in Chelmsley Wood.

METAL	SOIL	MIN.	MAX.	MEAN	STD. DEV.
Iron	T	7469	21667	15790	22.62
	S	11069	26115	15840	711.35
Lead	T	14	182	52.11	15.71
	S	3.5	190	38.54	13.49
Zinc	T	30	1124	173.5	55.86
	S	25	1092	108.3	55.58
Copper	T	15.2	581	49.63	24.94
	S	15.5	613	36.98	15.33
Chromium	T	22.5	179	40.41	17.09
	S	17.4	645	30.82	5.2
Nickel	T	5.35	42.35	18.47	0.56
	S	3.75	44.40	15.25	0.42
Cadmium	T	0	3.19	0.52	0.09
	S	0	1.90	0.35	0.03

Table 11.6 Mean and ranges of the soil metal concentrations (mg/kg)
(T = Topsoil : S = Subsoil)

11.4.1 Comparison of Topsoil and Subsoil Metal Concentrations

From consideration of Table 11.6 it can be seen that, with the exception of iron, the topsoil metal concentrations were greater than those of the subsoil samples. The decrease in metal concentration with depth has also been observed by a number of authors, including Lagerwerff and Specht (1970), Ward et al (1977), Farmer and Lyon (1977) and John (1972). The majority of the authors have suggested that the main source of heavy metals within the soils studied was aerial deposition (especially from vehicles), the addition of fertilizers and other anthropogenic sources from within the catchment area.

11.4.2 Comparison with 'Normal' levels

Through the comparison of the mean and range of measured total metal levels in Chelmsley Wood (Table 11.6) with the data from the literature (Table 11.2), a number of points were evident.

The lead concentrations measured in this study fell within the 'normal' range, but minimum levels were observed to be slightly higher (e.g. 3.5 compared with 2 mg/kg for subsoils and 14 mg/kg for topsoils). The maximum levels recorded were within the maximum 'normal' limits.

Levels of total zinc tended to be higher than those reported for uncontaminated soils. The maximum levels found were some three to four times greater than the upper limit for naturally occurring levels (i.e. 1124 mg/kg compared with 300 mg/kg). On comparison with Table 11.3, showing the guidelines for contaminated soils, suggested that the zinc values were indicative of heavily contaminated land.

However, it must be stressed that the range of concentration was considered and the highest value observed only occurred at one location, location F. The second highest value was 239.5 mg/kg, therefore all remaining samples fell within the uncontaminated class of soils. Similar comments apply for copper, where an extremely high value of over 600 mg/kg was observed at location F, indicative of highly contaminated land (Table 11.3). The second and third highest copper concentrations were of 330 and 174.5 mg/kg respectively. All other samples were below 60 mg/kg, the land can therefore be classified as uncontaminated.

Chromium concentrations tended to be low when compared with those for uncontaminated soil levels. Throughout the sampling period the minimum values were above those for uncontaminated land, however, the maximum levels obtained remained considerably lower than the maximum value of 3000 mg/kg stated for uncontaminated soils. In fact, all samples, with the exception of location G, remained below the common level of 100 mg/kg indicative of uncontaminated soils.

Nickel concentrations recorded in the Chelmsley Wood soils were indicative of naturally occurring levels, the majority of samples were close to the common level of 20 mg/kg.

Total cadmium content in soils is usually reported to contain between 0.1 and 2 mg/kg, with a common level of 0.1 mg/kg. All samples from Chelmsley Wood except for those for location F, were between 0 and 1.9 mg/kg.

Iron is the most commonly occurring heavy metal in soils and concentrations displayed great variation. Levels of iron found in the study were within the ranges quoted from contemporary studies.

The heavy metal content of soils within the study area, with the possible exception of location F, were within the quoted ranges for normal (unpolluted) soils and were therefore indicative of naturally occurring levels in soils.

11.4.3 Spacial Variation

The mean metal concentration for both topsoil and subsoil samples were calculated for each location, the results are presented in Table 11.7.

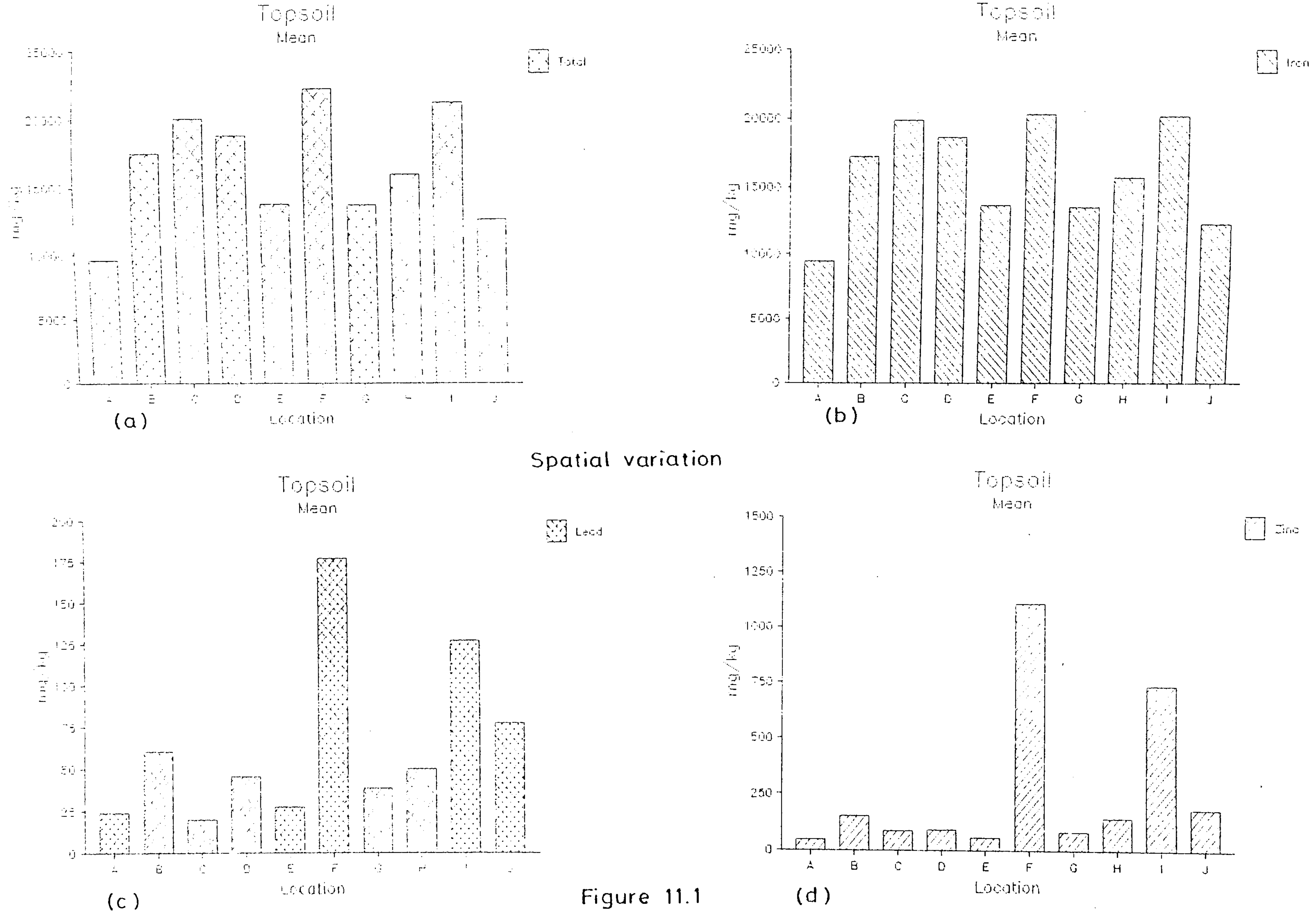
Figures 11.1 (a) and 11.2 (a) show the variation of total metals both within the topsoil and the subsoil respectively, over the catchment. Distribution of metals were not homogeneous across the catchment, some local variation was displayed. The topsoil peak concentrations occurred at location F and for the subsoils at location C.

Iron levels tended to be fairly uniform across the catchment (Figures 11.1 (b) and 11.2 (b)), the mean concentrations for the topsoil and subsoil were very similar, 16067 and 16138 mg/kg respectively. The peak iron concentrations occurred at location F for the topsoil and at location C for the subsoil.

Lead levels appeared to be more randomly distributed over the catchment (Figures 11.1 (c) and 11.2 (c)) than those of iron, with larger variations. Peak concentrations were observed at location F for both soil types.

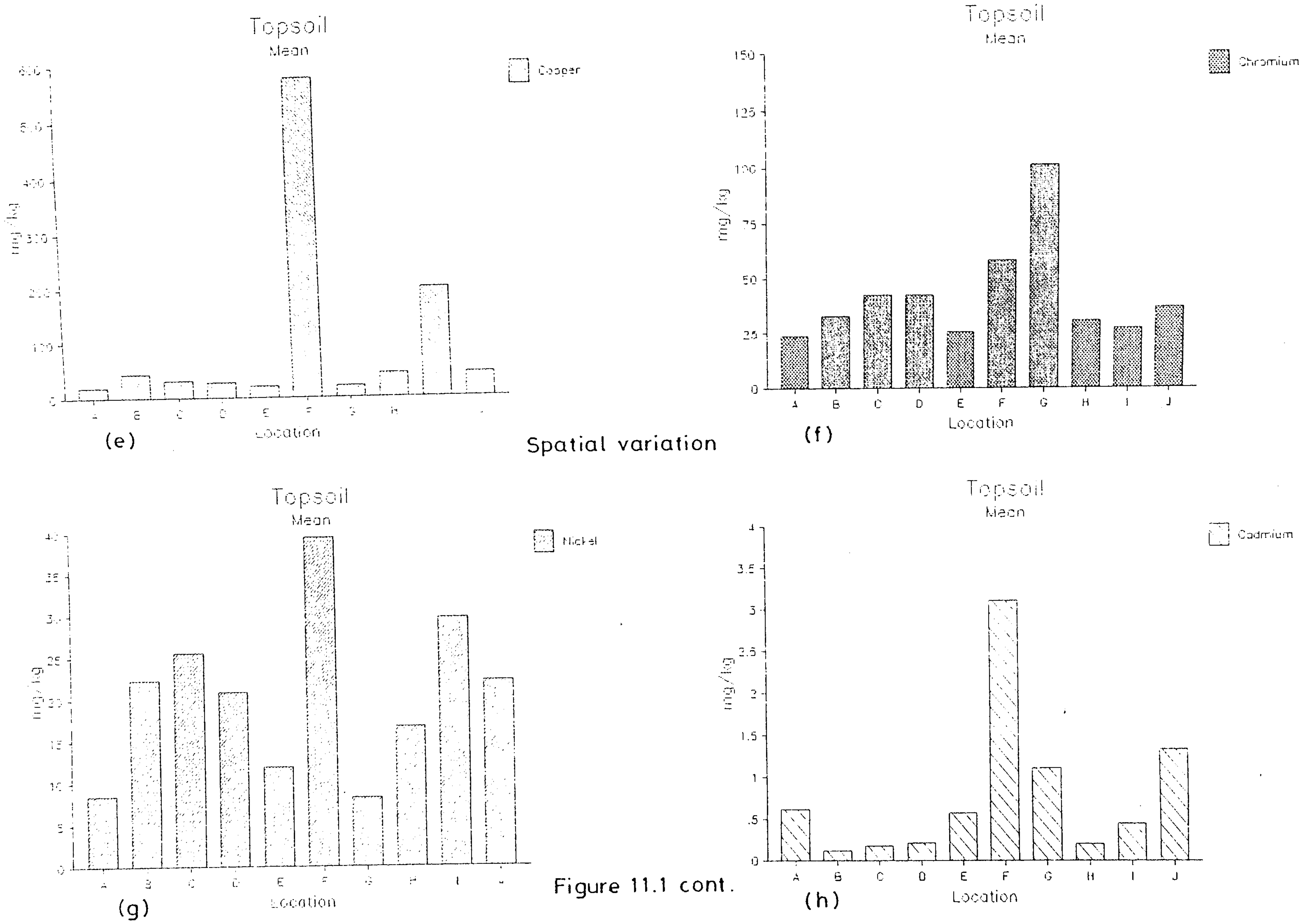
LOCATION		IRON	LEAD	ZINC	COPPER	CHROMIUM	NICKEL	CADMIUM
A	T	9467	23.50	48.00	18.02	23.67	8.45	0.61
	S	14604	34.25	77.00	20.87	31.87	17.27	0.39
B	T	17226	60.25	150.25	42.97	32.95	22.32	0.11
	S	17210	54.75	134.75	100.75	31.65	21.12	0.16
C	T	19827	19.50	83.75	30.52	42.57	25.55	0.17
	S	21433	18.25	128.50	31.05	38.15	20.87	0.08
D	T	18585	45.50	90.75	27.92	42.50	20.97	0.21
	S	16460	26.25	71.75	25.05	32.15	18.50	0.15
E	T	13675	27.25	55.25	19.85	25.82	11.95	0.57
	S	20062	7.50	44.00	15.65	17.45	6.40	1.01
F	T	20266	177.50	1102.25	577.90	58.25	39.57	3.09
	S	17462	110.50	566.00	316.27	44.57	28.75	0.80
G	T	13488	38.00	80.75	20.85	100.97	8.25	1.10
	S	11735	48.00	85.75	23.80	41.20	9.80	0.12
H	T	15715	49.75	142.25	43.60	30.95	16.75	0.19
	S	16253	35.50	74.50	41.55	29.35	13.72	0.16
I	T	20113	127.25	731.00	200.10	27.40	29.82	0.44
	S	12008	62.75	209.00	43.70	21.32	14.62	0.62
J	T	12305	77.50	180.50	43.88	36.92	22.16	1.32
	S	14155	58.50	164.00	33.75	35.49	15.90	0.45
Mean	T	16067	64.60	266.47	102.56	42.20	20.58	0.78
	S	16138	45.62	155.52	65.24	32.32	16.70	0.40
St.dv.	T	3742	50.85	356.17	175.55	23.05	9.80	0.91
	S	3148	28.99	152.62	91.42	8.33	6.26	0.32

Table 11.7 Mean soil metal concentrations (mg/kg).
(T = Topsoil : S = Subsoil)



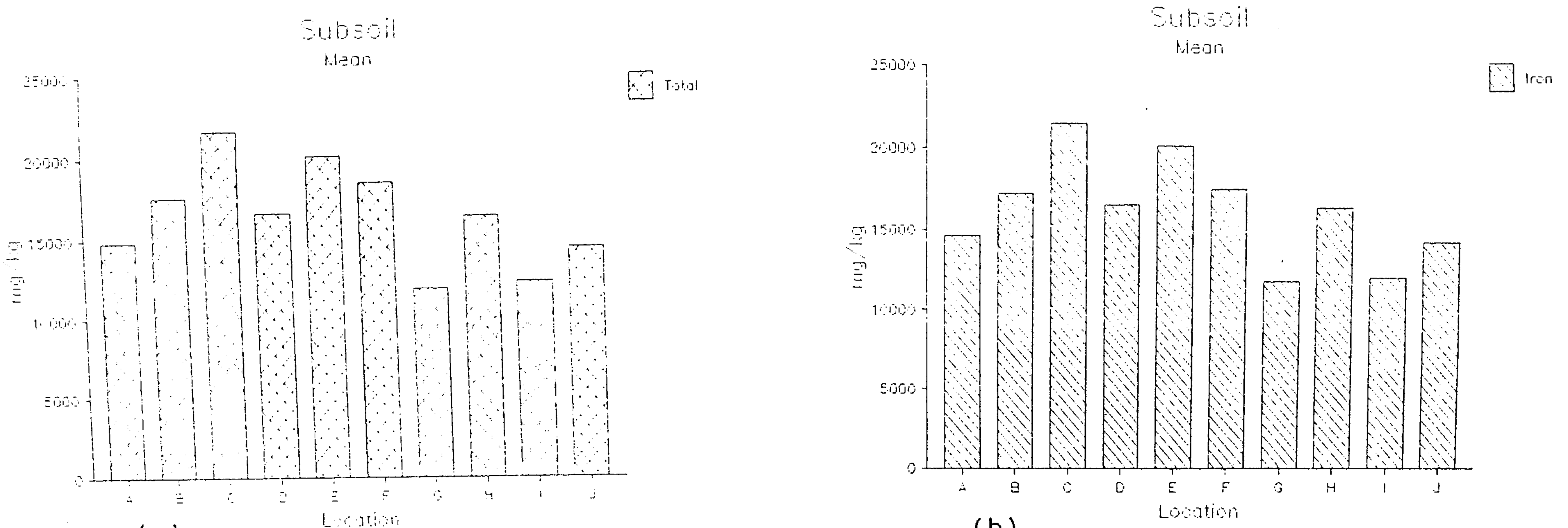
Spatial variation

Figure 11.1



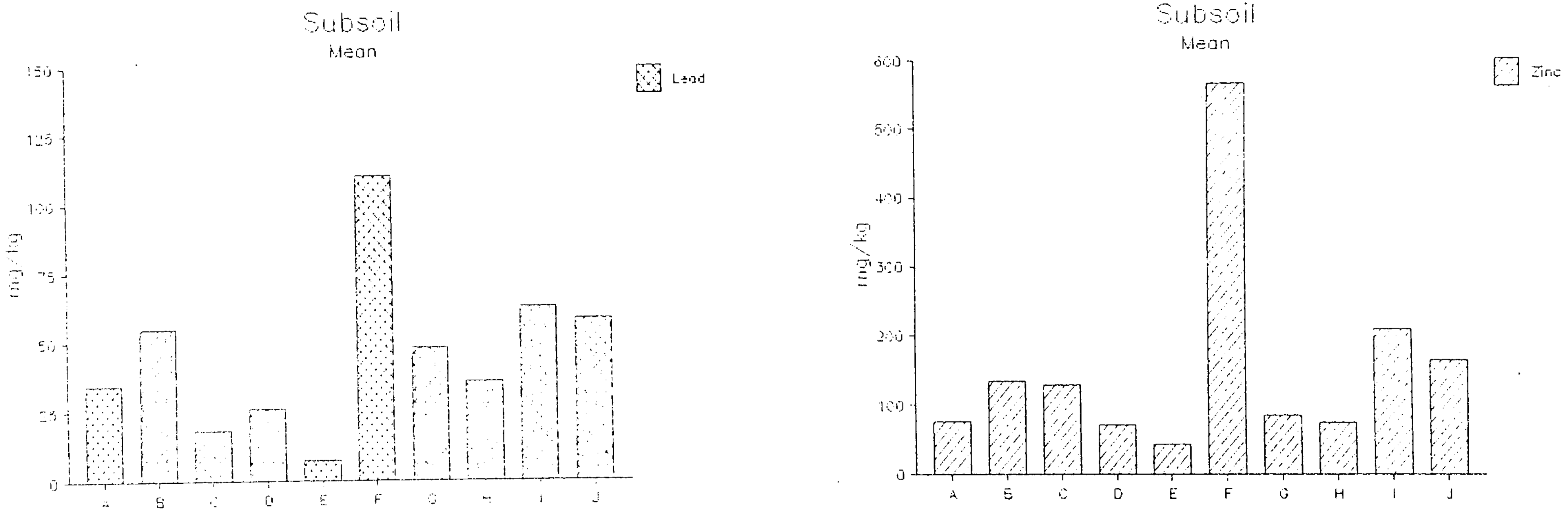
Spatial variation

Figure 11.1 cont.



(a) (b)

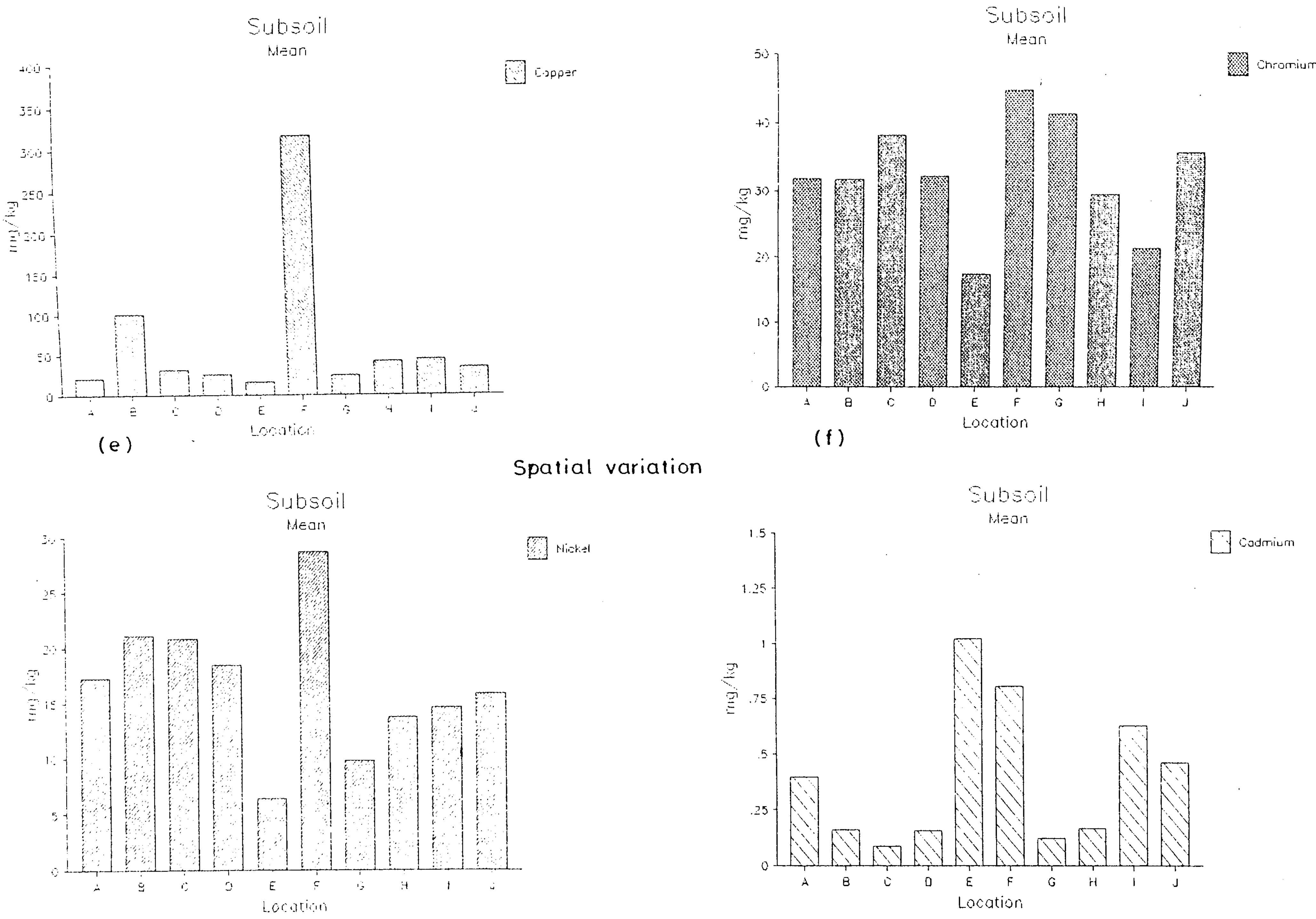
Spatial variation



(c) (d)

Figure 11.2

Spatial variation



(e)

(f)

(f)

(g)

Figure 11.2 cont.

Samples from location I had the second highest lead concentration of 127.25 mg/kg and 62.75 mg/kg, for the topsoil and subsoil respectively. The location was situated the nearest to a major road than any of other sampling station and would therefore be expected to contain elevated lead levels due to its proximity to the road. Location J had above average lead levels, this site was also located in close proximity to a road. All other sampling sites were located in secluded areas away from the effects of any major road and were shown to contain lower lead concentrations.

Zinc and copper concentraions were also elevated at location F (Figures 11.1 (d) and 11.2 (d) and Figures 11.1 (e) and 11.2 (e) for topsoil and subsoil respectively). The topsoil concentrations were seen to be some four to five times greater than the mean concentration (i.e. 1102.25 mg/kg for zinc and 578 mg/kg for copper). The second highest topsoil concentration was found at location I, as was lead, suggesting a common source for all of these metals (which may have been vehicle related). The subsoil copper concentration (Figure 11.2 (e)) at this location was lower than the average, substantiating the hypothesis that the metal contamination at this location could have been a result of aerial depostion from vehicles.

Topsoil nickel concentrations displayed the same general pattern to that of zinc and copper, (Figure 11.1 (g)). The peak concentration was observed at location F (approximately 40 mg/kg) followed by location I (approximately 30 mg/kg). A similar pattern was also seen for the subsoils (Figure 11.2 (g)), with a peak concentration of approximately 30 mg/kg at location F, but this was then followed by locations B and C, which had higher nickel concentrations than location I.

Chromium concentrations were fairly constant across the catchment (Figures 11.1 (f) and 11.2 (f)), with a peak topsoil concentration of 101 mg/kg occurring at location G, approximately twice the overall mean value. The second highest concentration was seen at location F (58.25 mg/kg). The reverse was true for the subsoil samples with peak concentrations occurring at location F followed by location G.

Peak topsoil cadmium concentrations also occurred at location F (Figure 11.1 (h)), whilst peak subsoil concentrations occurred at location E (Figure 11.2 (h)), with values of 3.1 and 1.01 mg/kg respectively. Above average concentrations were also observed at locations G and J.

The majority of metals within the soil samples were found to have highest concentrations at location F, the soils at this location were indicative of land that was slightly contaminated (in the case of cadmium) to heavily contaminated (in the case of zinc and copper).

The site at which these samples were taken was a shrubbery close to some recently constructed Old People Homes. The soil was very peaty and of a different nature to that found elsewhere within the catchment. It can therefore be deduced that it was probably transported into the area during construction and may have been contaminated elsewhere. The soil may have been imported from industrial or heavily trafficked areas (with the addition of road salt, vehicle emissions and metal containing pesticides used to protect roadside grasses and vegetation) or from contaminated dried sludge.

If samples from location F are excluded from the analysis then the levels of metal contamination across the catchment would be more uniform and indicative of naturally occurring levels.

Additionally, lead, zinc and copper showed above average concentrations at location I, especially within the topsoil. This was the only site which was close to any major road, hence the elevated metal levels found therefore suggest a likely source would be vehicles.

Low concentrations of metals were observed at location E. The samples from the site were taken from a secluded and shaded shrubbery in the grounds of Bosworth Wood School. Little human activity was observed at this particular location, the likelihood of any serious metal contamination from anthropogenic sources, such as vehicles and litter etc., was therefore limited.

Average concentrations for the majority of metals occurred at locations B and H.

11.4.4 Comparison of Spacial Variability in Soils to those within Road Sediments and Deposition

No direct comparison could be made between the soil, road sediment and deposition samples because the sampling points were not identical. However, some general observations were evident.

Lead concentrations within the topsoil and road sediments were correlated at a couple of locations, namely F and J (Figures 8.4 and 8.3), where above average concentrations for both topsoils and road sediments were observed. These could be attributed to vehicular activity within the vicinity.

Zinc and copper levels for both the topsoil and road sediments were predominantly below average within the centre of the catchment, which may have been due to reduced traffic flows and human activity within the immediate area.

Above average chromium levels were experienced on the western side of the catchment, for both topsoil (locations G and F, Figure 8.4) and road sediments (locations 11, 12 and 13, Figure 8.3). This general pattern was also observed for cadmium, with an additional higher than average concentration occurring at location J for the topsoil and location 5 for the road sediment.

Few correlations were evident for the deposition, soil and road sediments. However, one noteable observation was seen at location 12, where above average iron and lead concentrations were found for both the deposition and the road sediments, which were also related to the elevated levels of the metals in the topsoil at location F.

Above average chromium levels were observed at location F and G in the topsoil and at location 12 and 16 for the road sediment and deposit cannister samples. The higher deposition rates at these locations may have contributed to the higher concentrations of metals found within the soils and hence the road sediments.

Unfortunately, no other distinct correlations were evident from the available data.

11.4.5 Metal Proportions

The relative proportions of each metal to the total metals in each soil sample were calculated and expressed as a percentage. Average values are presented in Table 11.8 and graphically in Figure 11.3 (a) and (b).

Iron was seen to predominate in the road sediment samples, as was the case for the deposit cannisters. For the soil samples the percentages were even higher with mean values of approximately 98% for both the topsoil and subsoil, compared with 78% for the deposition and 92% for the road sediment samples.

Since iron dominated all samples and tended to mask the proportions of the other metals, percentages excluding iron were calculated. The average results are given in Table 11.9 and Figures 11.3 (c) and (d).

Zinc was now seen to predominate in both topsoil and subsoil samples with a mean percentage of approximately 44%, which was followed by lead (17% for topsoil and 16% for subsoil) then copper, chromium, nickel and finally cadmium, the latter of which had a mean percentage of 0.2%.

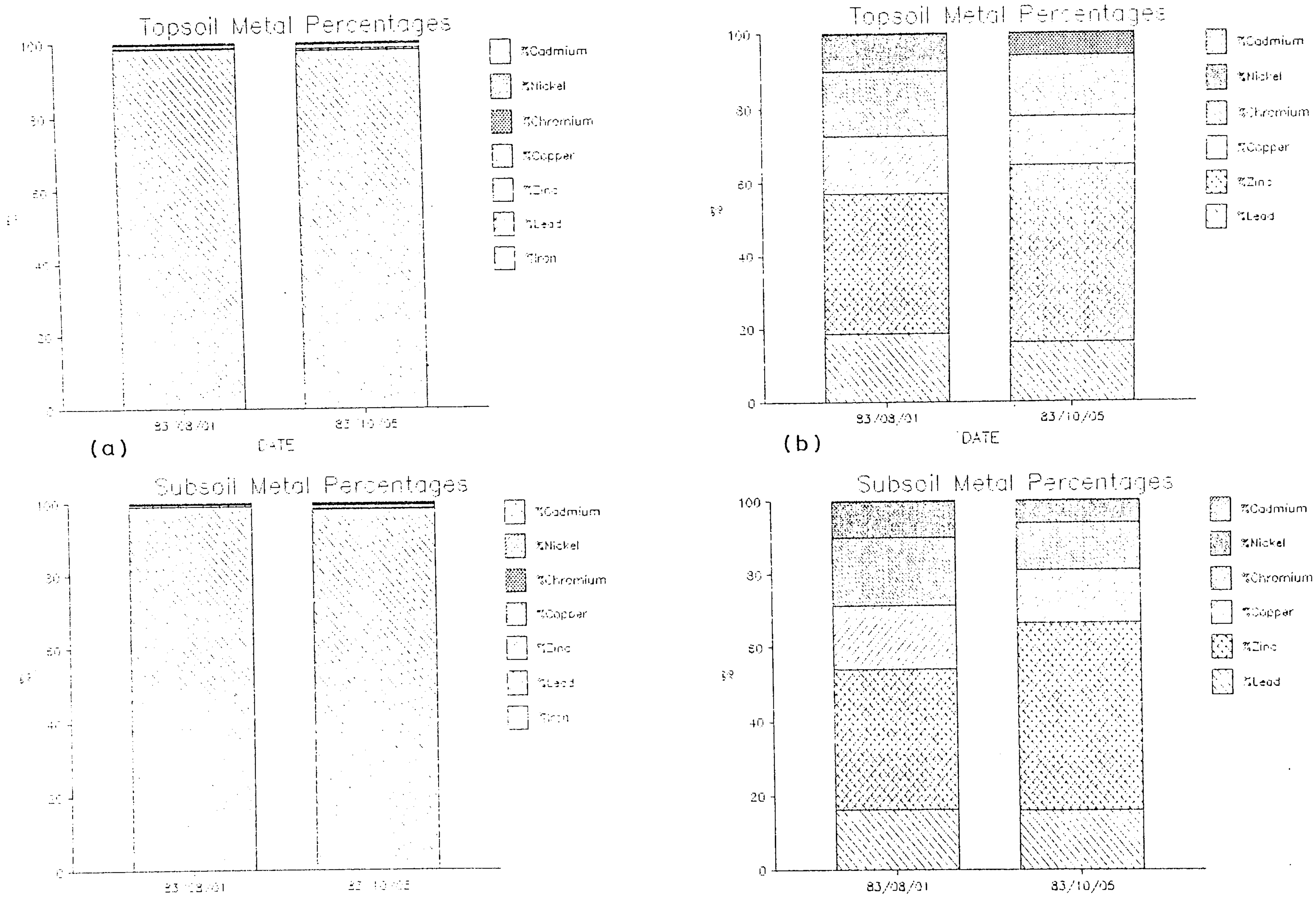
The proportions of metals in the topsoil and subsoil were very similar which reflected the small variations in metal concentrations between the two soil types.

DATE		PERCETAGES						
		IRON	LEAD	ZINC	COPPER	CHROMIUM	NICKEL	CADMIUM
01/08/83	T	98.45	0.26	0.77	0.195	0.176	0.105	-
	S	98.86	0.20	0.48	0.169	0.167	0.091	-
05/10/83	T	97.97	0.37	1.21	0.357	0.328	0.107	0.0004
	S	98.08	0.32	0.95	0.291	0.224	0.094	-
Mean	T	98.21	0.32	0.99	0.276	0.252	0.106	0.0002
	S	98.47	0.26	0.716	0.230	0.195	0.092	-

Table 11.8 Mean soil metal proportions including iron.
(T = Topsoil : S = Subsoil)

DATE		PERCETAGES					
		LEAD	ZINC	COPPER	CHROMIUM	NICKEL	CADMIUM
01/08/83	T	18.61	38.42	15.66	17.21	9.84	0.21
	S	16.18	37.88	17.28	18.63	9.80	0.19
05/10/83	T	15.96	48.75	13.20	16.23	5.59	0.24
	S	15.86	50.62	14.56	12.85	5.84	0.23
Mean	T	17.28	43.58	14.43	16.73	7.71	0.22
	S	16.02	44.25	15.92	15.74	7.82	0.21

Table 11.9 Mean soil metal proportions excluding iron.
(T = Topsoil : S = Subsoil)



(a) (b) (c) (d)

Figure 11.3

11.4.6 Metal Correlations

Correlation matrices were computed to examine relationships between any two metals within the soil samples. These were calculated for the mean values of both topsoil and subsoil for each sampling period.

Within the first batch of topsoil samples, high correlations were observed between lead and all of the other metals apart from iron, the highest correlation of which was between lead and cadmium with a correlation coefficient (r) of 0.97 (see Table 11.10). Good correlations were also seen between zinc and copper, zinc and nickel, zinc and cadmium and between nickel and cadmium. The correlations may reflect a common source of the metals.

Only a few good correlations were observed within the second batch of soil samples, with high correlations between iron and nickel ($r = 0.83$), lead and zinc ($r = 0.94$), lead and copper ($r = 0.90$) and the most significant of which was between zinc and copper with a correlation coefficient of 0.99.

The first batch of subsoil samples displayed only one significant positive correlation, between zinc and lead ($r = 0.87$). A fairly high negative correlation was also observed between iron and lead ($r = -0.80$). The second batch of subsoil samples displayed more correlations similar to those observed for the first batch of topsoil samples. High correlations were seen to occur between lead and zinc ($r = 0.92$), lead and copper ($r = 0.93$), lead and nickel ($r = 0.83$), zinc and copper ($r = 0.98$), zinc and nickel ($r = 0.92$) and also between copper and nickel ($r = 0.93$). The most significant correlation was observed between zinc and copper ($r = 0.98$).

METAL	Iron	Lead	Zinc	Copper	Chromium	Nickel	Cadmium
Iron	1.0						
Lead	0.27	1.0					
Zinc	0.46	0.92	1.0				
Copper	0.40	0.88	0.87	1.0			
Chromium	0.41	0.85	0.72	0.90	1.0		
Nickel	0.66	0.88	0.94	0.83	0.78	1.0	
Cadmium	0.23	0 .97	0 .88	0 .94	0.90	0.83	1.0

Table 11.10 Correlation matrix for the topsoil of 01/08/83.

The mean correlation matrices for both topsoil and subsoil samples displayed three distinct correlations, in all cases the correlation coefficient was greater than 0.90. The correlations were between lead and zinc, lead and copper and zinc and copper. Within the mean subsoil data set significant correlations were found between zinc and nickel and copper and nickel, with correlation coefficients of 0.82 and 0.85 respectively.

The only consistent correlations observed throughout the data set were those between lead and zinc, lead and copper and zinc and copper. This probably reflects a common source for the three metals, which may have been from the actual parent rock material or from some extraneous source such as motor vehicles. The presence of these metals in motor vehicle pollutants together with their subsequent deposition and accumulation within the soil profile has been previously identified (Lagerwerff and Specht (1970)).

CHAPTER 12

THE ANALYSIS OF STORMWATER RUNOFF DATA

12.1 Storm Hydrographs

12.1.1 Introduction

The contribution of land surface derived heavy metals to the toxicity of stormwater runoff in urban areas is now well documented (Wilber and Hunter (1975, 1977 and 1979), Hedley and Lockley (1975), Pope et al (1979), Nightingale (1975) and Pitt and Amy (1973)). Although there is a substantial body of literature attributing total metal loadings to urban non point sources, little attention has been paid to the detailed temporal characteristics of metal loadings during specific storm hydrographs, one of the intentions of the research outlined in this thesis was to study this aspect of stormwater quality. The quality of stormwater has been shown to vary greatly during the course of an event and as a result differences between events, even at different times of the year, are often masked. The temporal variation of metal concentrations during a storm show distinctive patterns for each individual storm and this feature will now be discussed in detail for the Chelmsley Wood catchment.

12.1.1.1 Flow

Fifteen runoff events were monitored for flow and heavy metal concentration during the period August 1983 to July 1984. One of these events was spring runoff from snowmelt (storm 10, 22/01/84), but the remainder were all rainfall/runoff events resulting from between 0.8 and 8.4 mm total rainfall. Runoff was generally characterized by a single or double peak flow shortly after the start of a runoff event. The time to reach the peak runoff, after the initial rise to a level triggering the sampler ranged from zero minutes for a thunderstorm, to 151 minutes for a long double peaked storm, and 94 minutes for the snowmelt event. The maximum flowrate recorded during the monitoring period was 2012.54 litres per second (l/sec).

A baseflow was also found to occur at the sampling station during dry weather periods. The baseflow rates were much lower than those observed during storm events, and averaged 20 litres per second. The source of the baseflow could have been either groundwater, which had infiltrated the storm sewer system, or from illegal connections made to the surface water sewer system. However, the latter was assumed to be negligible due to the recent construction of the system. Throughout the stormwater analyses the average metal content of the baseflows were subtracted from the stormwater data.

12.1.1.2 Heavy Metals

Of the heavy metals analysed in this study, iron, lead and zinc predominated in the runoff from the rainfall and snowmelt events, with concentrations of total iron at times exceeding 15 mg/l and those of lead and zinc at times exceeding 2 mg/l and 1 mg/l respectively.

The observations made for the particulate and soluble metal phases during the individual events will now be discussed in detail. The pollutographs for each individual storm event are included in the following discussion, where sws corresponds to the particulate metals and sww the soluble metals. The total metal concentrations will not be discussed in great depth since they are a combination of the particulate and soluble metals analysed and therefore tend to mask any change between the two phases. Where the Phox instrument was operating the results are included in the discussion.

12.1.2 Storm 1 (16/08/83) (Figure 12.1)

The flow was characterized by a single rounded peak reaching a maximum flowrate of 212.5 l/sec 12 minutes after the start of the storm (i.e. taken as the the time the sampler was initiated at a flowrate of 90 l/sec).

Most of the particulate metals peaked at 15 minutes and then decreased throughout the rest of the storm. Cadmium, however, peaked later, at 28 minutes, with a value of approximately 0.01 mg/l. Chromium showed a second peak at this time, whilst chromium, nickel and cadmium displayed further small peaks 40 minutes into the storm.

The values for soluble metals displayed a less distinct pattern of behaviour than those for the particulate metals. Lead and iron peaked 15 minutes into the storm, with values of 9 and 13 mg/l respectively, while zinc displayed a slightly later peak at 18 minutes with a concentration of 1.3 mg/l. The maximum copper levels were attained between 12 and 15 minutes into the storm with values of 0.225 mg/l. Soluble chromium, nickel and cadmium concentrations appeared to be somewhat erratic and showed no distinct behavioural trends.

12.1.3 Storm 2 (16/09/83) (Figure 12.2)

For storm 2 the flow was characterized by a sharp peak of 586 l/sec 12 minutes after the start of the storm.

The particulate metals tended to display double peaks where the first peak appeared to be greater in magnitude than the second. However, the metal peaks did not occur at the same point in time. Iron initially peaked at 12 minutes with a concentration of 7 mg/l whilst the following second peak occurred at 18 minutes (5.65 mg/l).

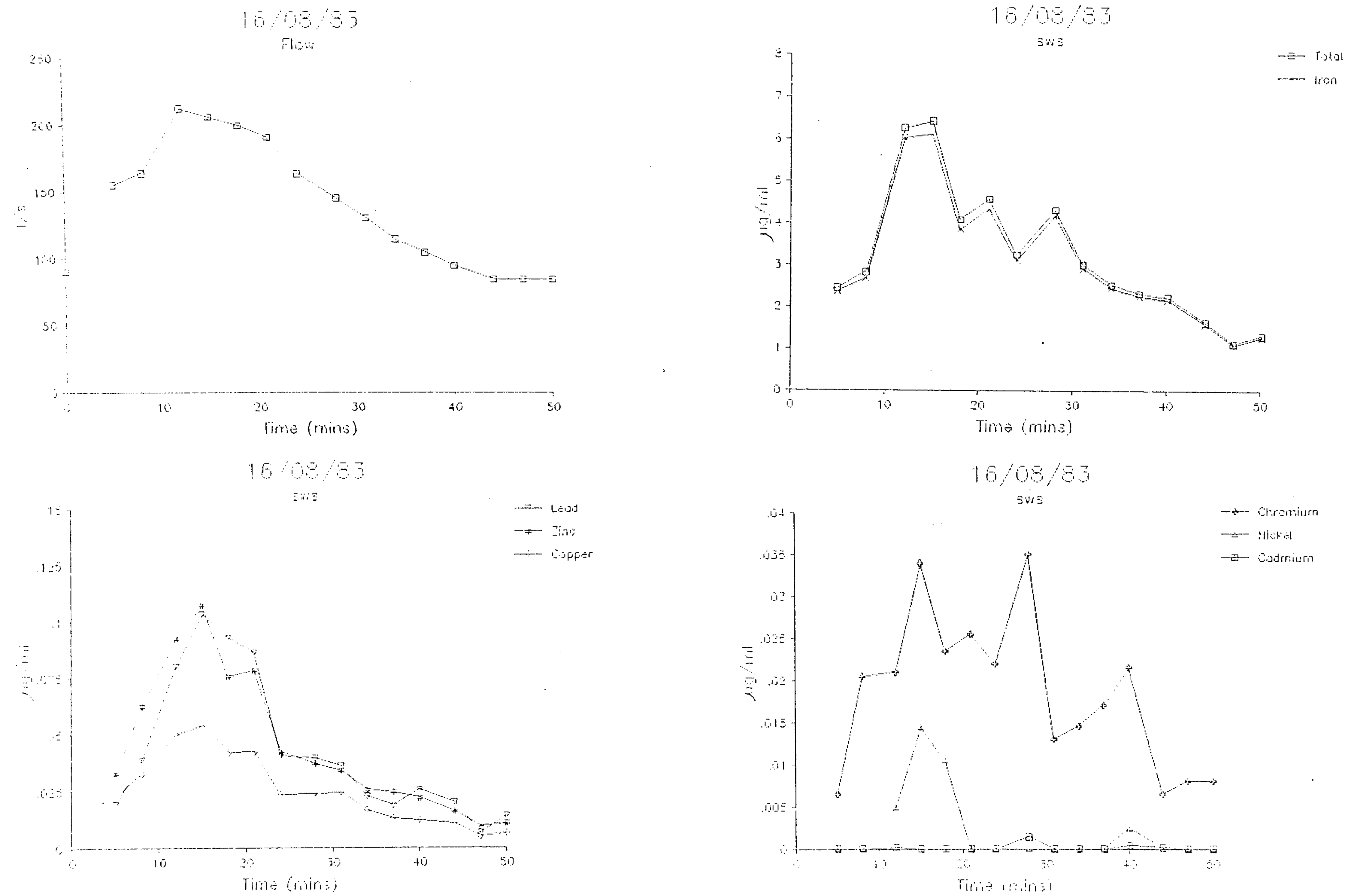
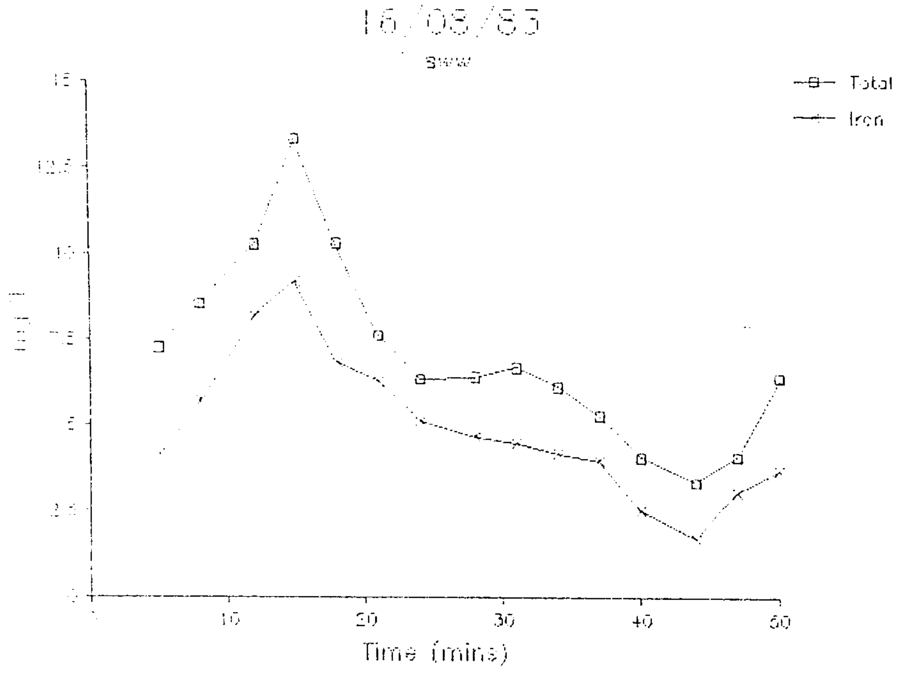
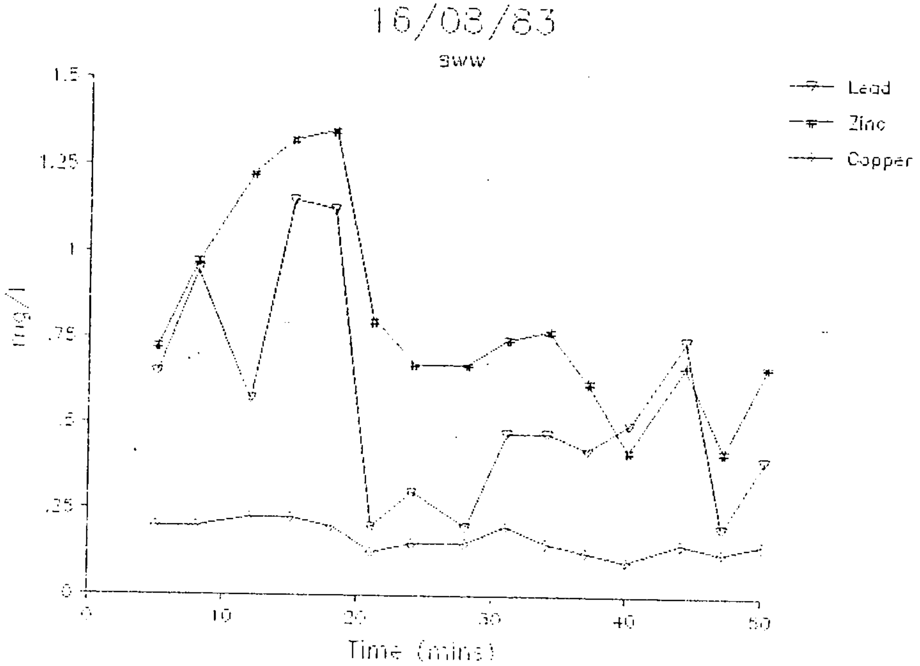


Figure 12.1 Pollutographs for Storm 1.





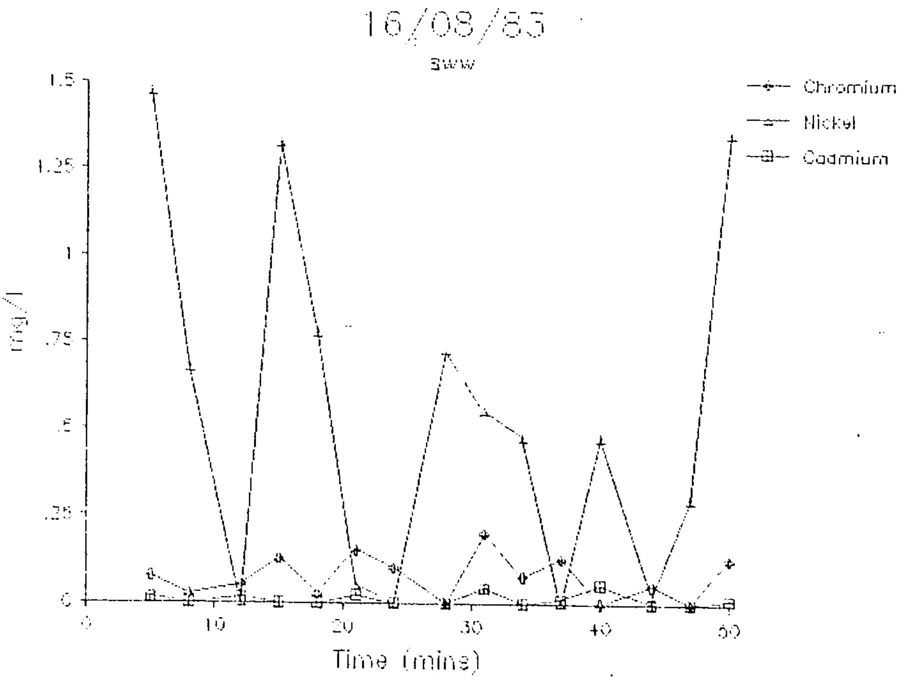


Figure 12.1 cont.

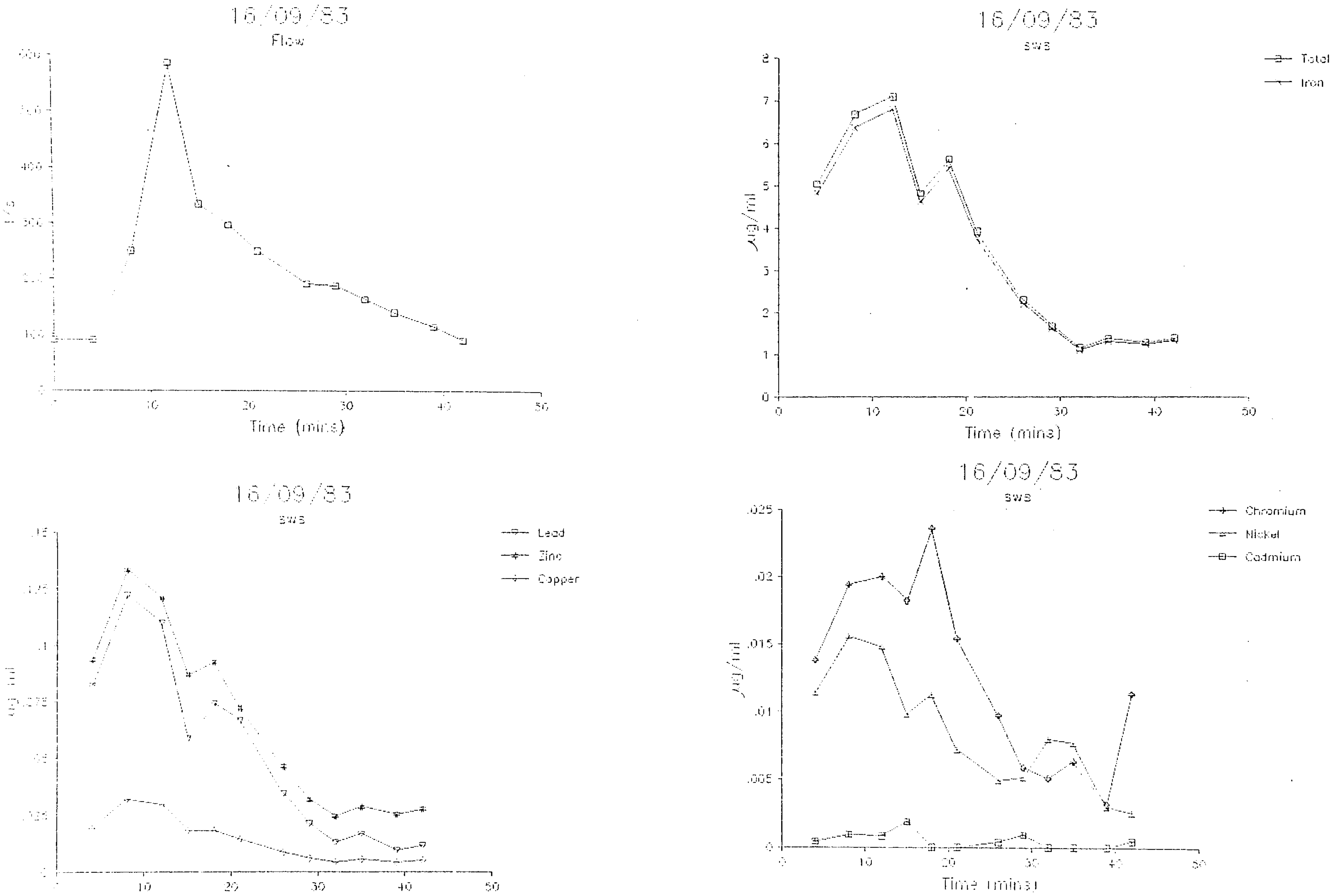


Figure 12.2 Pollutograph for Storm 2.

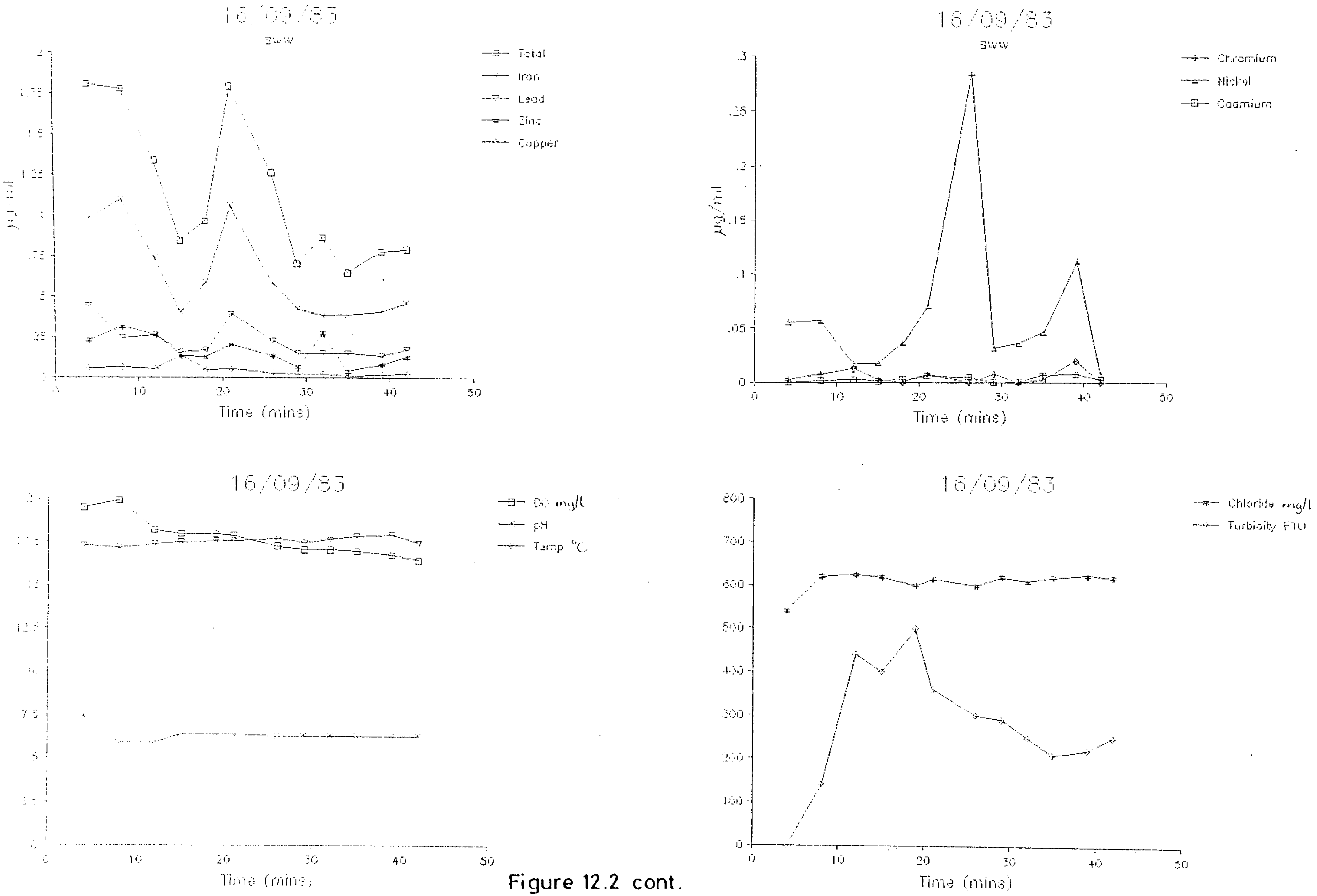


Figure 12.2 cont.

The concentration then decreased for the rest of the storm. Lead, zinc, copper and nickel first peaked at 8 minutes, 4 minutes before that of iron, while the second peak appeared at 18 minutes into the storm, as was the case for iron. Chromium displayed a peak later into the storm at a time of 18 minutes and a concentration of 0.024 mg/l, and cadmium peaked at 15 minutes with a value of 0.18 mg/l.

The majority of soluble metal concentrations tended to be high at the start of the sampling period and then decreased to a minimum at 15 minutes and subsequently increased to a second peak at 21 minutes. The maximum iron levels were found to be 1.8 mg/l at a time of 21 minutes. Lead concentrations were highest at the start of the storm and also displayed a later peak at 21 minutes with a value of 0.4 mg/l. Zinc displayed three peaks at 8, 12 and 32 minutes with concentrations of 0.31, 0.2 and 0.275 mg/l respectively. Copper concentrations showed one main peak at 15 minutes when other metals were at a minimum level. Chromium and cadmium each displayed a single peak much later into the storm, after 39 minutes, whilst nickel showed two large peaks at 26 and 39 minutes.

Data from the Phox system, which was operating at the time, is also shown in Figure 12.2. Dissolved oxygen levels peaked, with a value of 20 mg/l, after 8 minutes and then gradually decreased throughout the rest of the storm. The maximum value of pH was 7.4, which occurred at the start of the storm, it then decreased to 5.9 at 8 minutes and increased once more to a value of 6.4, after 11 minutes staying constant at this level for the remaining duration of the storm. The temperature remained virtually constant for the entire storm at 17 to 18^{o}C. The chloride concentration was lowest at the start of the storm with a value 540 mg/l, it then rose to a maximum of

620 mg/l at 8 minutes and then stayed fairly constant for the remainder of the storm. Turbidity levels were initially zero but increased rapidly to 440 FTU at 12 minutes and rose still further to 500 FTU after 18 minutes had passed. It then gradually decreased to a value of 250 FTU at the termination of the storm.

12.1.4 <u>Storm 3 (10/10/83)</u> (Figure 12.3)

The hydrograph for storm 3 displayed three distinctive peaks in increasing order of magnitude. The first peak occurred at 4 minutes with a flowrate of 140 l/sec, the second at 79 minutes with a flowrate of 366 l/sec and the third peak was observed at 129 minutes with a flowrate of 531 l/sec.

Multiple peaks were also seen to occur for the particulate metal concentrations, in several instances peaks for a number of metals coincided. As with the flowrate, the particulate metals displayed three major peaks. The total metal concentrations followed closely the pattern of iron.

Regarding particulate matter, the iron concentration pollutograph displayed three distinctive peaks at 10, 91 and 129 minutes with concentrations of 1.46, 0.96 and 0.75 mg/l respectively. Lead concentrations showed a number of rather erratic peaks, the highest value of which was 0.0225 mg/l at a time of 10 minutes. Zinc and copper concentrations displayed a similar pattern of behaviour to that of lead with peaks ocurring at 10 and 35 minutes into the storm, the concentrations for zinc being 0.013 and 0.0046 mg/l respectively, and those for copper being 0.0097 and 0.0028 mg/l respectively. Additional peaks were also observed at 91 to 95 minutes into the storm (as with lead) and at 135 minutes (after lead and iron). The largest

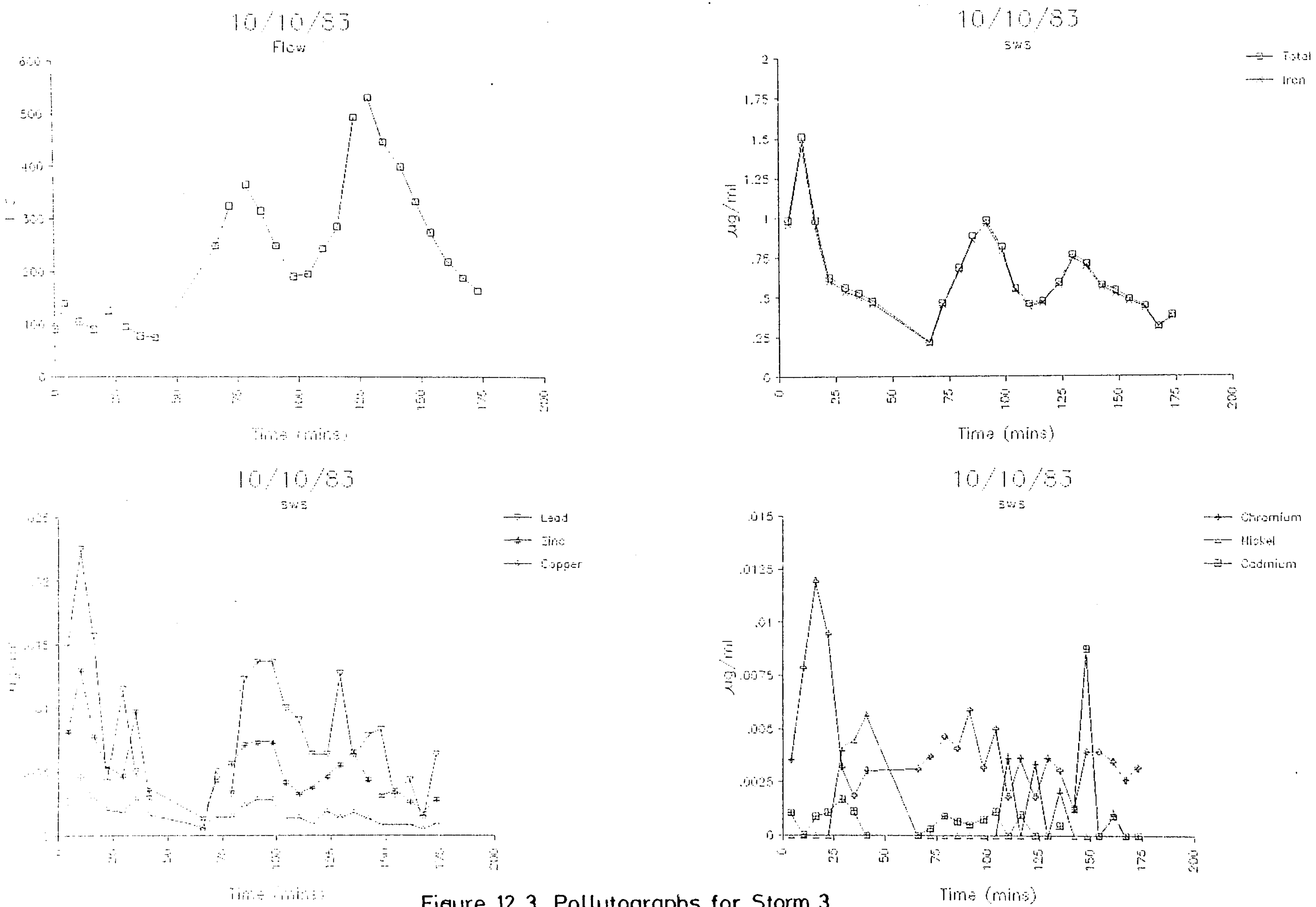
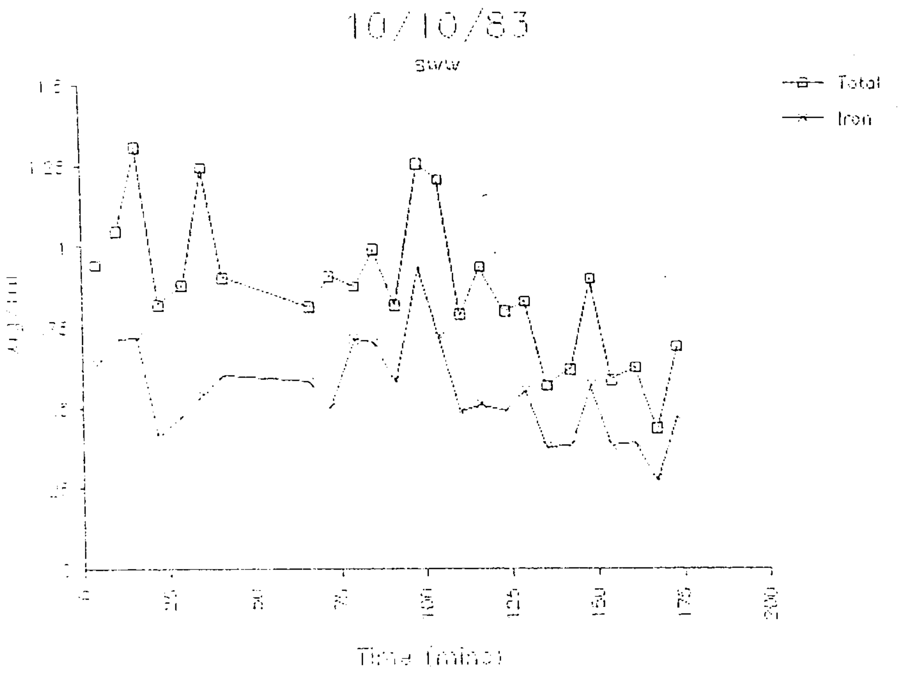
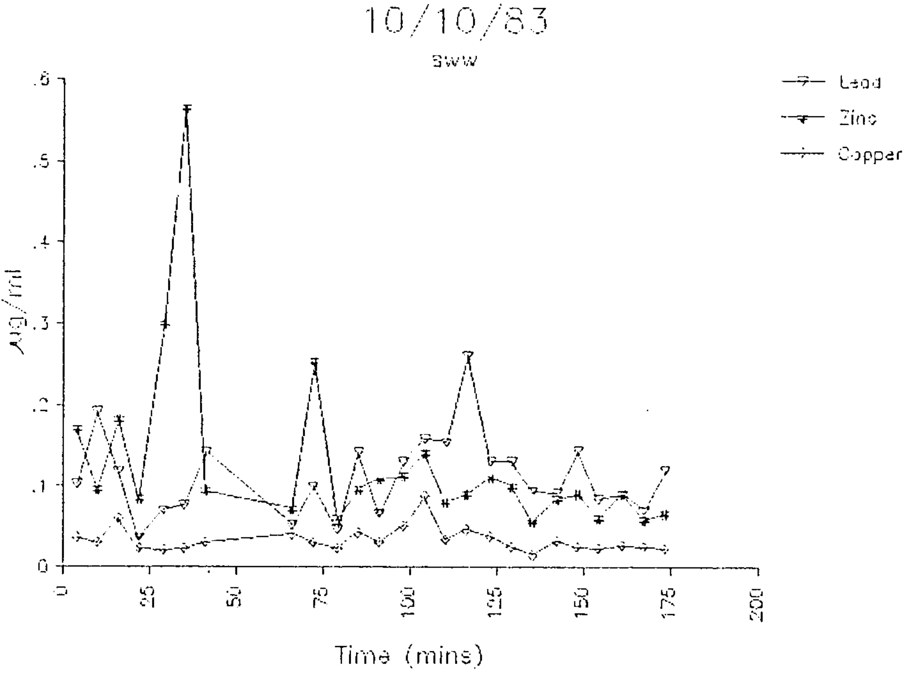
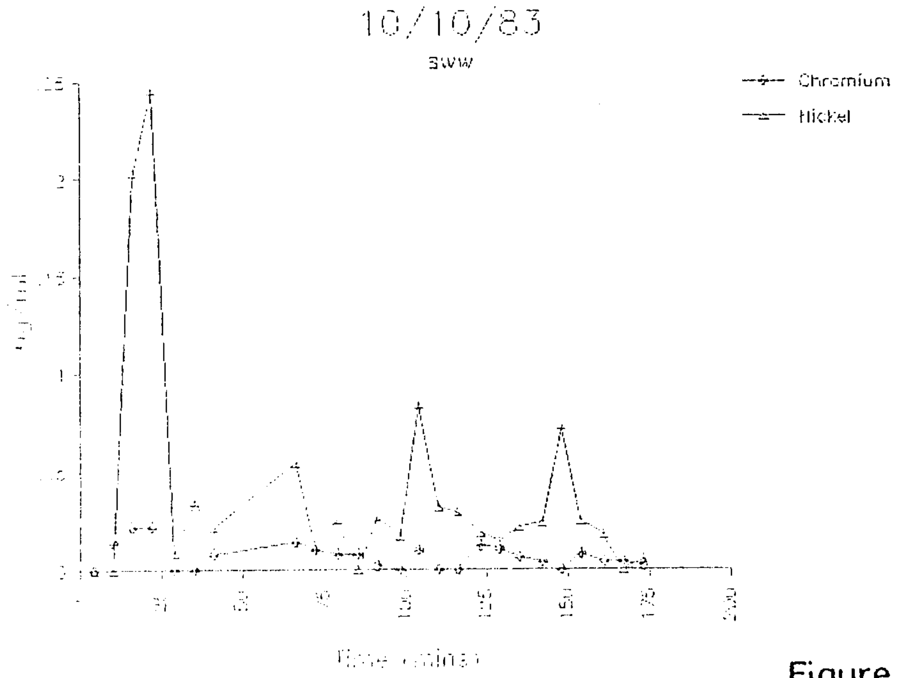


Figure 12.3 Pollutographs for Storm 3.







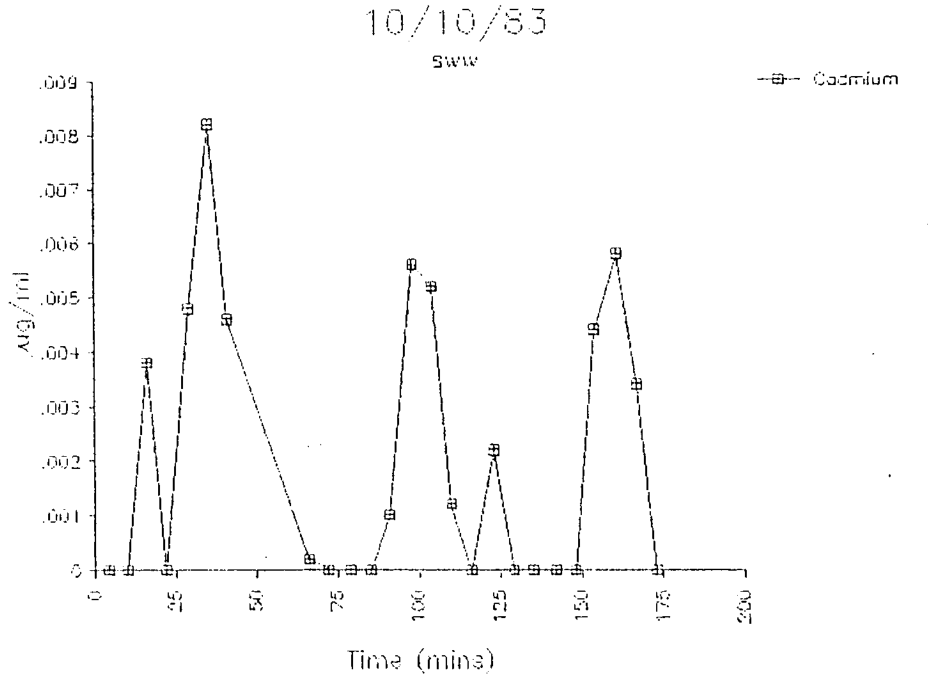


Figure 12.3 cont.

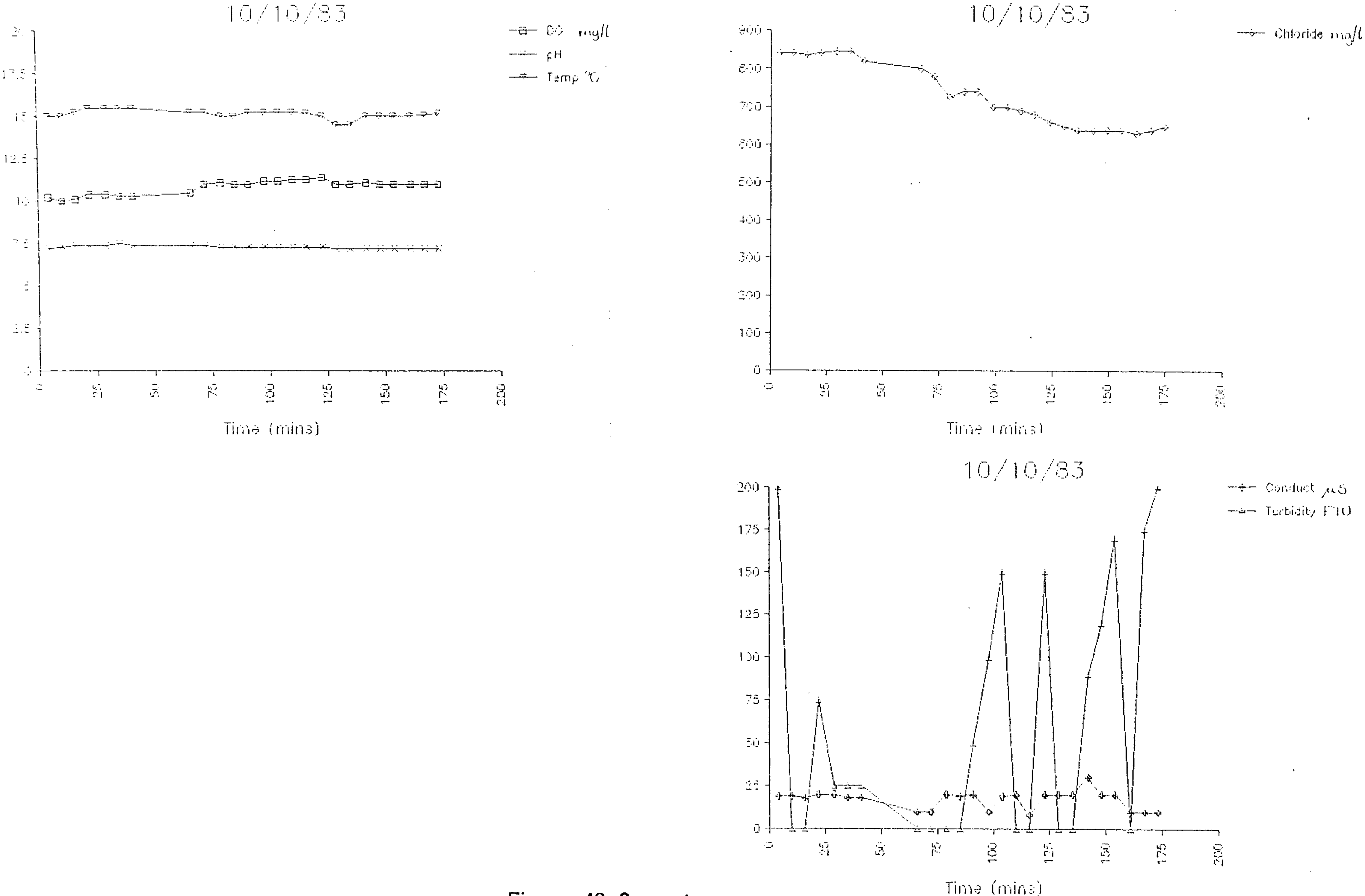


Figure 12.3 cont.

peak for chromium with a value of 0.012 mg/l occurred at a time of 16 minutes, after iron, lead, zinc and copper (at a time of 10 minutes). Concentrations of nickel appeared to display an erratic pattern of behaviour and the peaks that occurred did not coincide with any other metal. Cadmium displayed a very large peak late into the storm with a value of 0.009 mg/l at a time of 148 minutes.

No distinct pattern of behaviour was observed for the soluble metal concentrations, and a number of irregular peaks occurred for each metal. The largest peak value for iron concentration occurred 98 minutes into the storm with a concentration of 0.94 mg/l, and that for lead concentration of 0.262 mg/l, occurred at 116 minutes. Two very large peaks were observed for zinc concentrations at times of 35 and 72 minutes with corresponding values of 0.566 and 0.254 mg/l respectively. Copper concentration attained a peak value of 0.088 mg/l at 104 minutes into the storm. As was the case in the previous storm copper concentration followed a similar trend in behaviour to that of zinc. The highest values of chromium concentration were observed after 16 minutes, with a value of 0.022 mg/l, whilst the peak value of nickel concentration, 0.246 mg/l, occurred after 22 minutes. Cadmium concentration remained low and somewhat erratic throughout the duration of the storm. The maximum value of concentration recorded was 0.0082 mg/l at a time of 35 minutes.

The first flush phenomenon of heavy metals was observed in storm 2.

Dissolved oxygen, pH and temperature remained fairly constant throughout the duration of the storm, with values averaging 11 mg/l, 7.3 and 15°C respectively. The chloride concentration was initially high with a value of 840 mg/l but then subsequently decreased in value to 650 mg/l at the end of the storm period. Values of conductivity appeared to be somewhat irregular throughout the storm but tended to fall within the range of 18 to 20 µs. No distinct pattern could be seen in the values of turbidity, where an erratic behaviour was the norm for the whole storm period.

12.1.5 Storm 4 (02/11/83) (Figure 12.4)

A double peak was observed in the flowrate for storm 4. The first peak occurred within 4 minutes of the onset of sampling, with a value of 500 l/sec, and a second smaller peak of 300 l/sec occurred after 20 minutes, thereafter the flow decreased with time.

The particulate metal concentrations displayed one major peak at 27 minutes into the storm period, lagging the peak flowrates by 23 and 7 minutes respectively. Some of the particulate metal concentrations also showed additional peaks, which were observed to coincide with the particulate concentrations of other metals. The iron concentration showed one major peak at 27 minutes with a value of 29.45 mg/l, after which it rapidly decreased. Lead, zinc, copper, chromium and nickel were also observed to peak after 27 minutes with values of 0.84, 0.033, 0.15, 0.065 and 0.04 mg/l respectively. Additional peaks were seen for lead at 10 minutes and for chromium and nickel at 7 minutes. Cadmium levels were highest at the start of the storm.

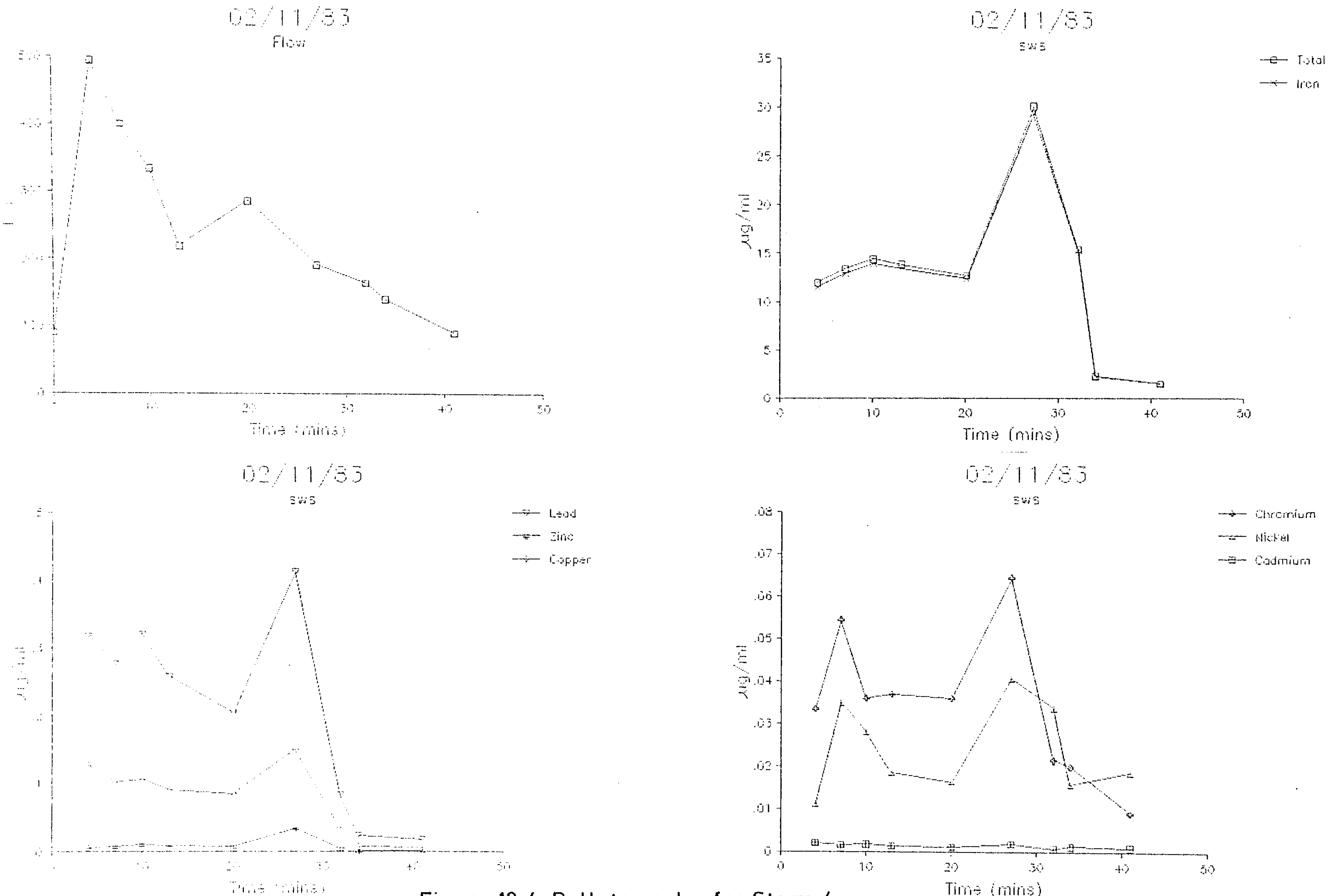


Figure 12.4 Pollutographs for Storm 4.

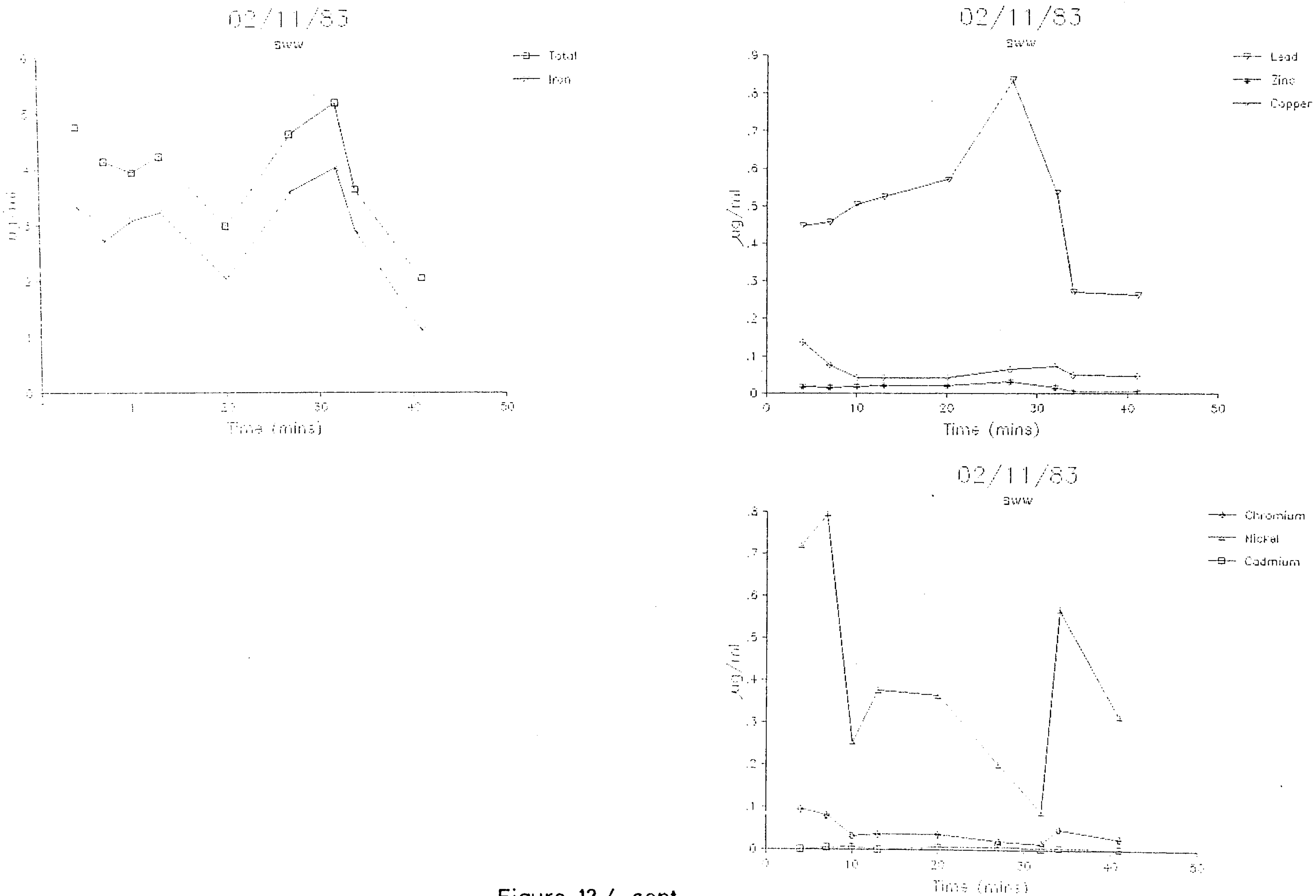


Figure 12.4 cont.

The soluble metals displayed some distinct patterns when compared with other storms analysed. The total metal concentration closely correlated with that of iron with the maximum iron concentration over 4 mg/l occurring after 32 minutes. Lead and zinc displayed earlier peaks within the storm period at 27 minutes with values of 0.84 and 0.032 mg/l respectively. Copper concentrations initially were at a maximum of 0.094 mg/l but thereafter decreased fairly rapidly during the first 5 minutes. Nickel concentrations showed two major peaks at 7 minutes, 0.796 mg/l, and 34 minutes, 0.57 mg/l. Cadmium concentrations remained low throughout the entire event but a slight increase occurred after 10, 27 and 34 minutes.

12.1.6 Storm 5 (03/11/83) (Figure 12.5)

The storm hydrograph for storm 5 displayed a small peak of 219 l/sec after 4 minutes followed by a even smaller peak at 23 minutes of 206 l/sec after which the flow decreased with time.

Each of the particulate metal concentrations exhibited one major peak. Iron, lead, zinc and copper concentrations peaked after 16 minutes with corresponding values of 2.34, 0.02, 0.001 and 0.0075 mg/l respectively. Lead concentration, however, displayed two smaller additional peaks at 29 and 42 minutes. Chromium concentration was seen to peak before all of the other metals with a value of 0.0405 mg/l at 10 minutes. Nickel concentrations were highest at the start of the storm, 0.018 mg/l, whereas maximum cadmium levels did not appear until the end of the storm.

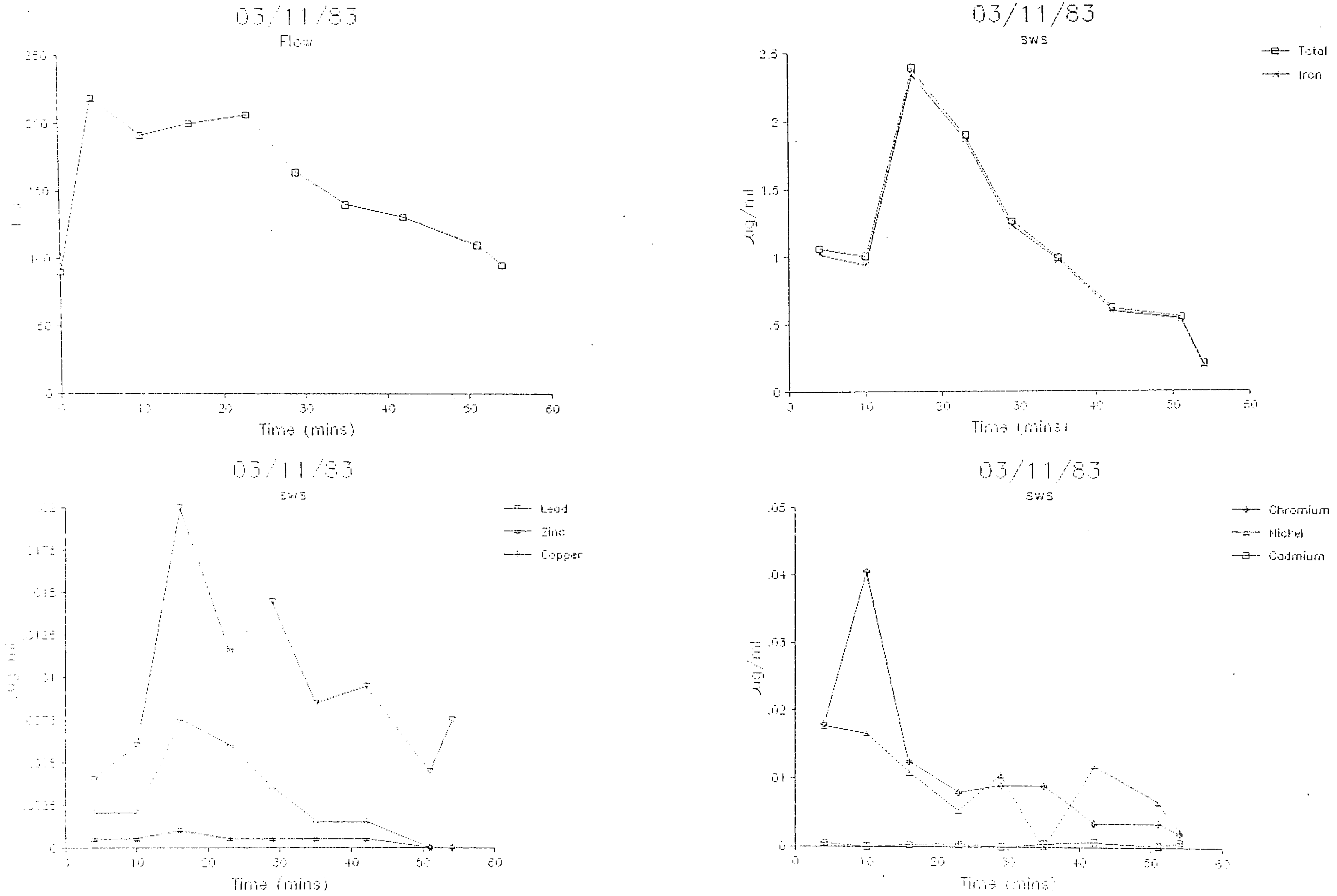


Figure 12.5 Pollutographs for Storm 5.

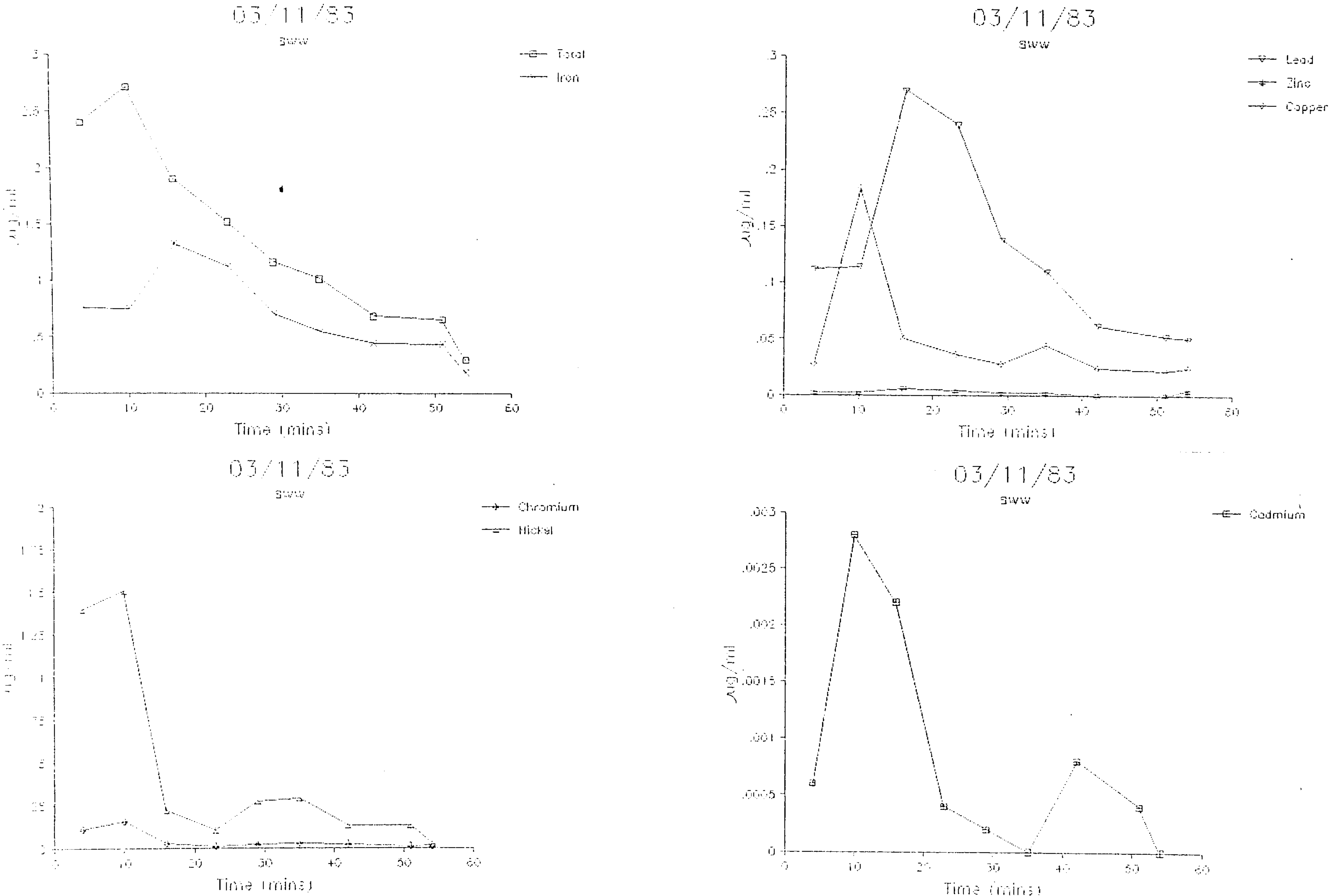


Figure 12.5 cont.

As was the case with the particulate metal concentration, the soluble metals each displayed one major peak, although at different times. Iron, lead and zinc concentration all peaked, with values of 1.328, 0.27 and 0.006 mg/l respectively, at a time of 16 minutes into the storm, as was the case with their sediment counterparts. However, copper, chromium, nickel and cadmium concentration peaked earlier at a time of 10 minutes. Cadmium concentration displayed an additional secondary peak at 42 minutes with a value of 0.0008 mg/l.

On the whole an overall decrease in all metal concentrations were observed throughout the duration of the storm event.

12.1.7 Storm 6 (25/11/83) (Figure 12.6)

The storm was of a long duration with a corresponding hydrograph duration of 170 minutes. There was, however, a break in the sampling cycle between 70 and 94 minutes when the flow dropped below 90 l/sec. It will, however, be treated within this study as one storm, but in two parts. The initial part of the storm was characterized by fairly low flowrates, with the peak flowrate of 145 l/sec occurring after 26 minutes. The second part of the storm was more intense with a much steeper peak attaining a value of 450 l/sec at 151 minutes.

The majority of the particulate metals displayed their highest concentrations at the start of the sampling period and those subsequently declined during the latter stage of the first part of the storm. This observed behaviour could have been due to the fact that there was a very rapid response in the sewer, which was not picked up directly by the sampling equipment and therefore the first part of the storm discharge was lost.

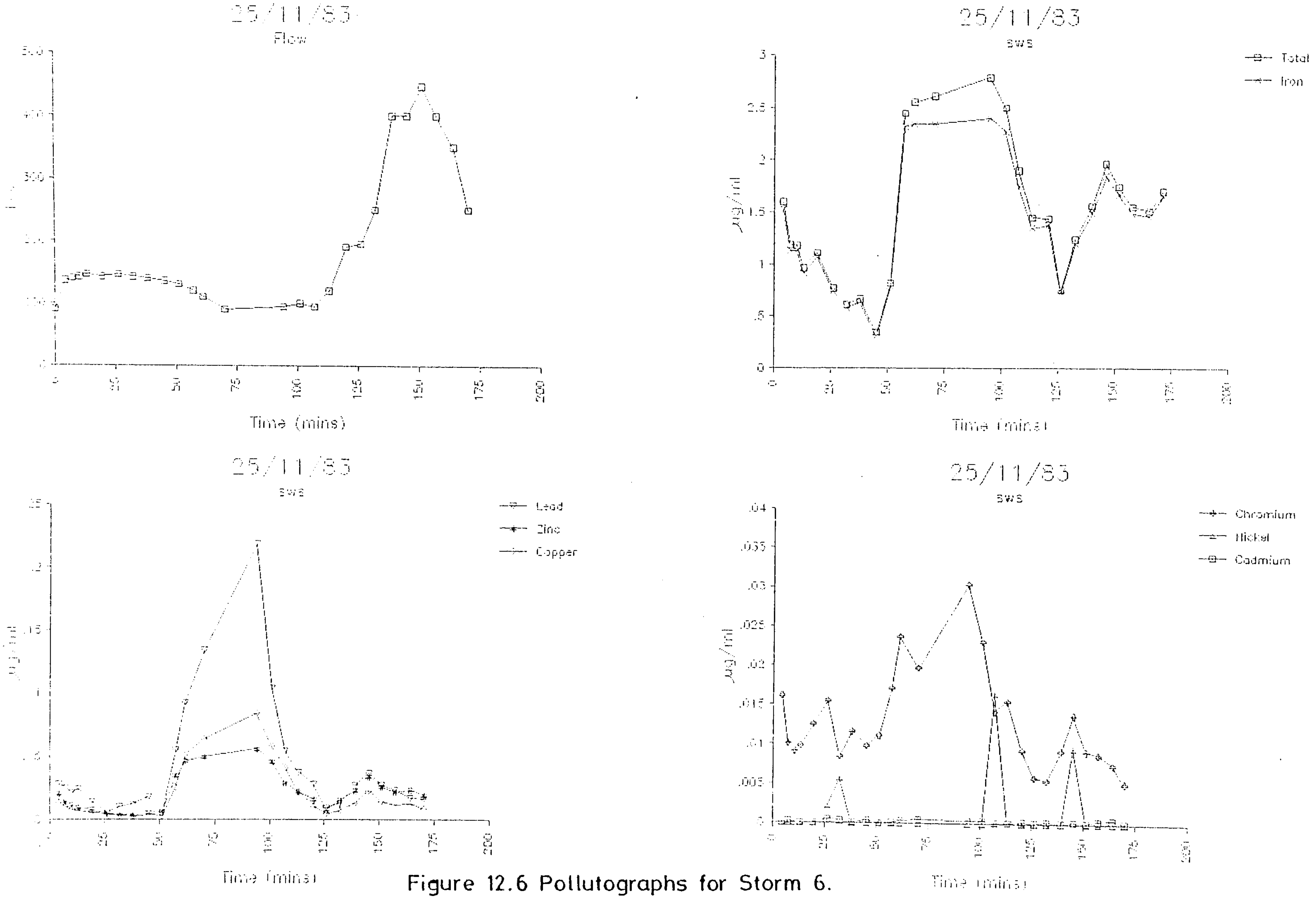
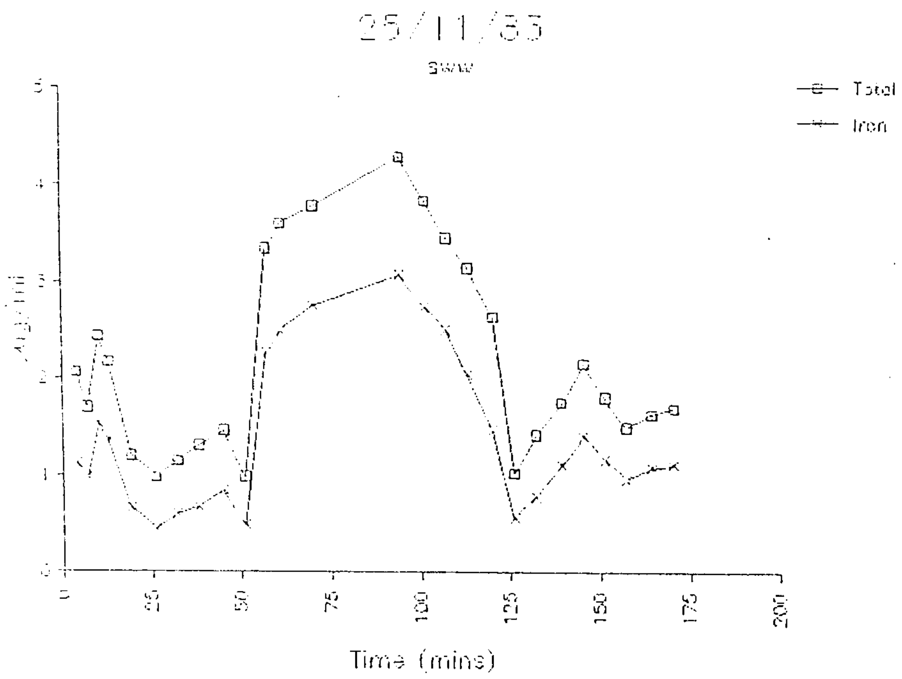
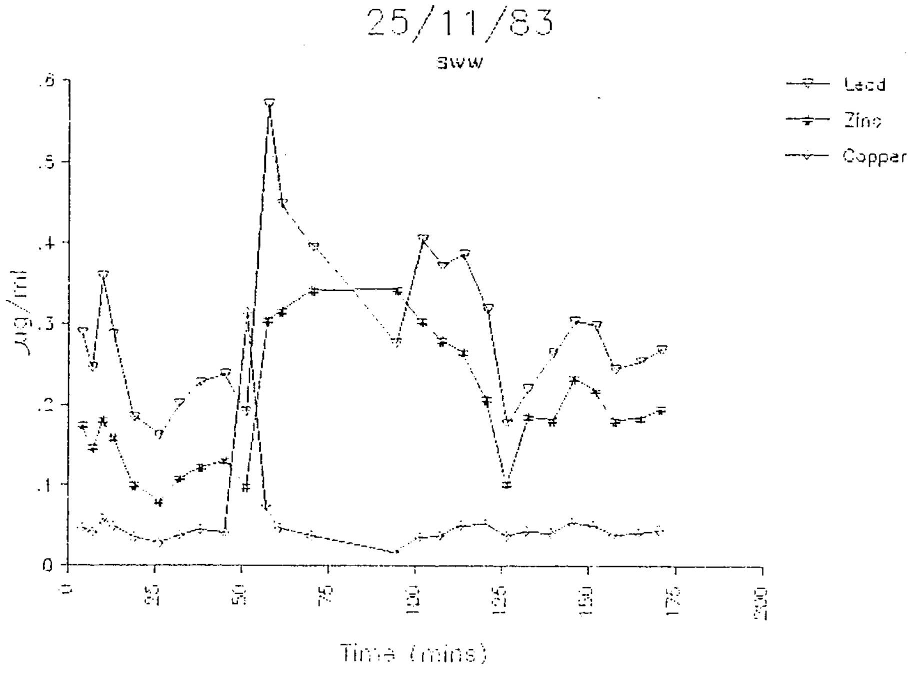


Figure 12.6 Pollutographs for Storm 6.





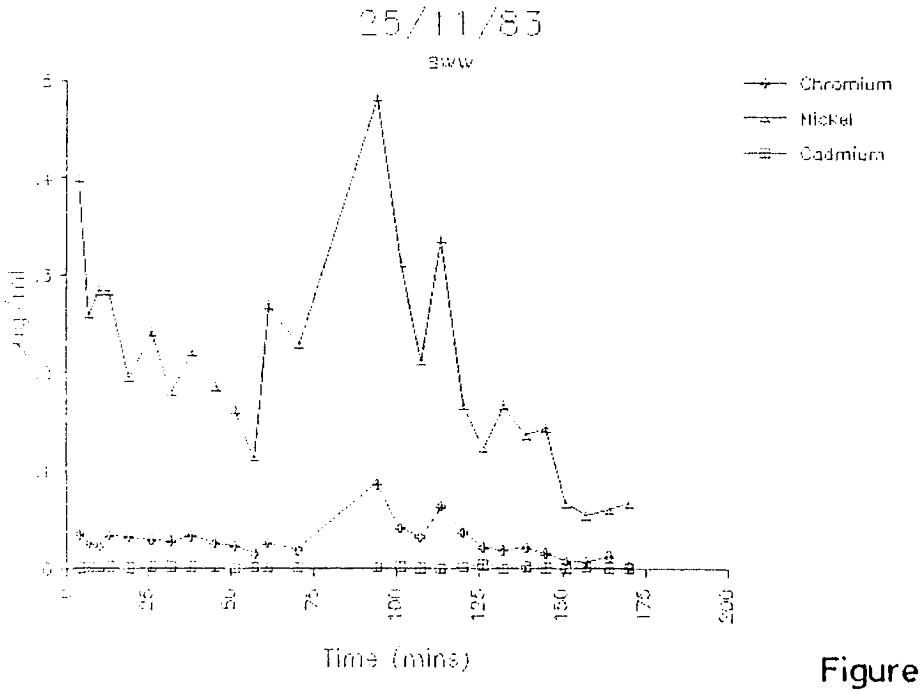


Figure 12.6 cont.

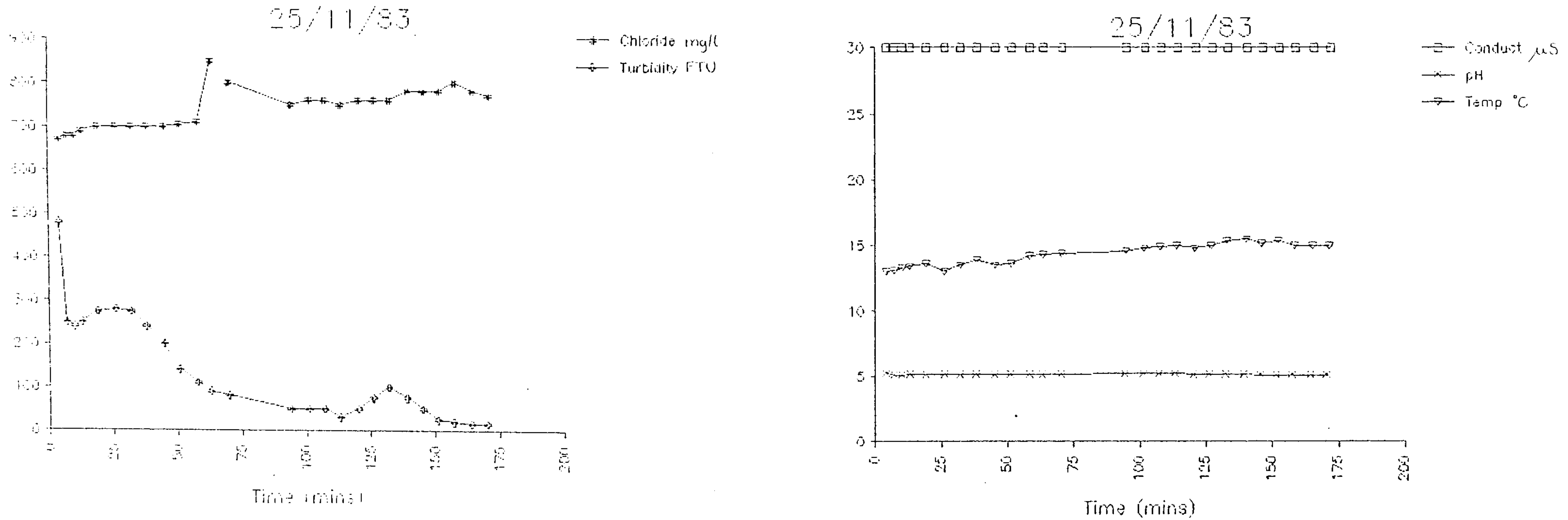


Figure 12.6 cont.

The concentration of iron particulates decreased in value initially and then later rose, both during the latter stages of the first part of the storm and also during the initial phases of the second part of the storm, where a maximum value of 2.4 mg/l was attained at 94 minutes. Thereafter the iron concentration declined in value and reached a smaller secondary peak of approximately 1.7 mg/l at 145 minutes. The remaining heavy metals also displayed a secondary peak at a time of 145 minutes. Lead, zinc, copper and chromium concentration peaked at 94 minutes, i.e. at the start of the second phase of the storm, as was the case with iron. Nickel concentration displayed three distinct peaks at 32, 107 and 145 minutes with corresponding values of 0.0056, 0.016 and 0.0137 mg/l respectively. The highest particulate cadmium concentrations were observed at 26 and 70 minutes with concentrations of 0.00043 and 0.00048 mg/l respectively.

The soluble metal concentrations displayed an overall trend of variation similar to that of the particulate metal concentrations. Iron, zinc, chromium and nickel peaks were observed at 94 minutes. The lead concentration peaked at an earlier time of 61 minutes and before copper reached its maximum after 57 minutes. In fact there tended to be an inverse relationship between copper and the other metals at this time. The highest cadmium concentration, 0.004 mg/l, was seen later on in the storm event at a time of 126 minutes.

A general statement for the overall pattern of behaviour experienced by the metal concentration would be that the particulate metal concentration tended to decrease towards the end of the storm whilst the soluble metals tended to increase.

Values of pH and conductivity remained fairly constant throughout the duration of the storm, with values of 5 and 30 μs respectively, whilst the temperature increased slightly from 13 to 15°C. Chloride concentrations continually increased throughout the duration of the storm event, attaining a peak value of 850 mg/l at 61 minutes. Maximum values for turbidity, 480 FTU, were reached at the start of the sampling event but during the first 3 minutes rapidly decreased to 250 FTU and reached a minimum of 15 FTU at the end of the storm.

12.1.8 Storm 7 (17/12/83) (Figure 12.7)

Low flowrates were observed throughout the entire event for storm 7. The initial discharge was 90 l/sec which then gradually decreased to 75 l/sec. Normally the trailling end of the storm would not be sampled, but during this event the probe within the sewer must have been moved and fell slightly deeper into the stormwater stream. The concentration of metals remained low throughout the entire the storm.

The particulate metal concentration varied throughout the event but no distinct trend or pattern of behaviour could be observed. Iron concentration was highest at the begining of the storm with a value of 0.55 mg/l and attained an additional later peak of 0.50 mg/l at a time of 19 minutes. Zinc, copper and cadmium concentrations peaked 6 minutes into the runoff event whilst chromium peaked later at 16 minutes.

The majority of soluble metal concentrations displayed two peaks, the second generally being higher than the first. Iron, lead and zinc concentrations were observed to peak at 10 and 19 minutes into the storm. Copper concentrations remained fairly constant throughout the event and nickel showed one peak value 0.056 mg/l after 10 minutes.

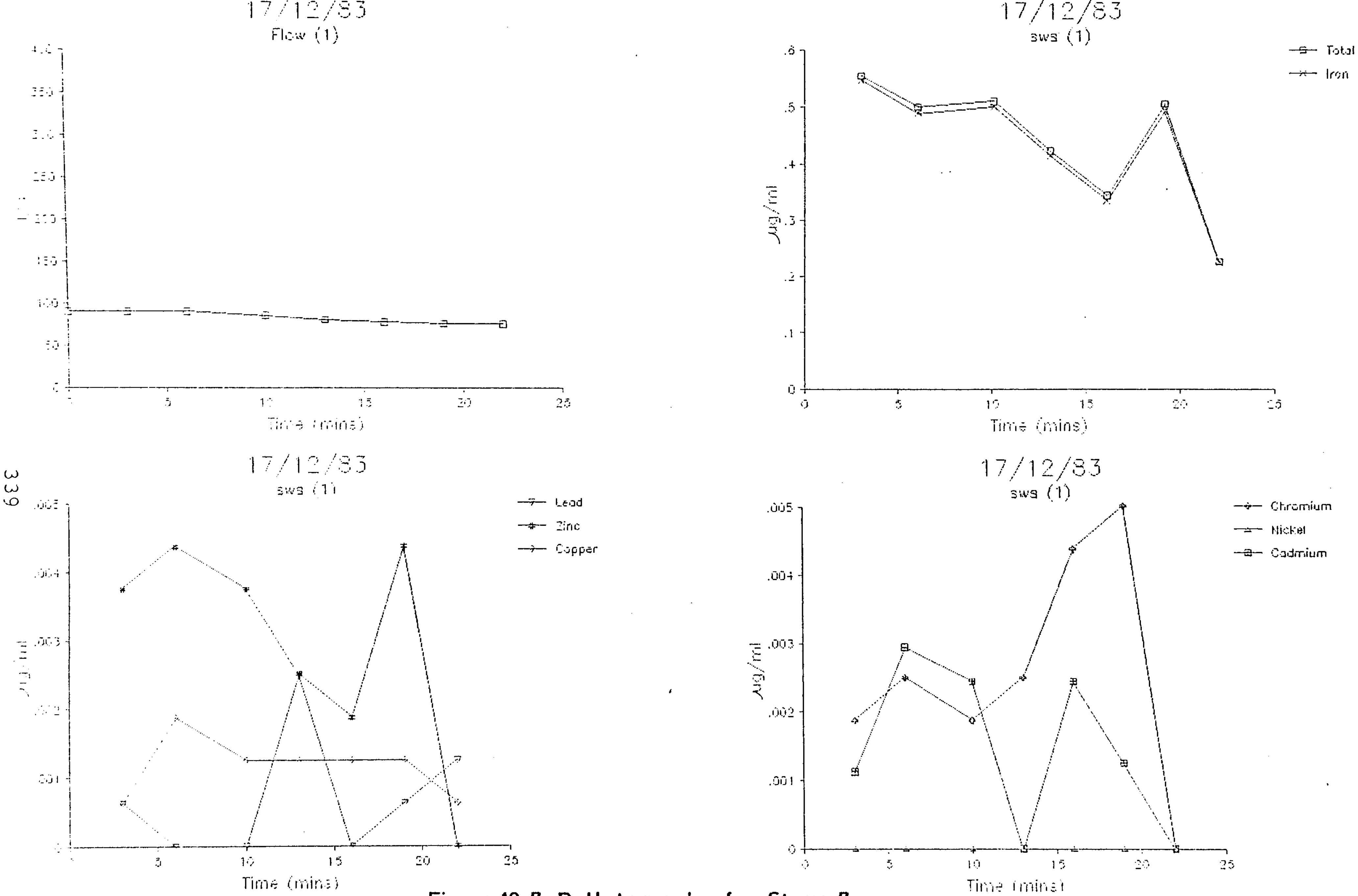
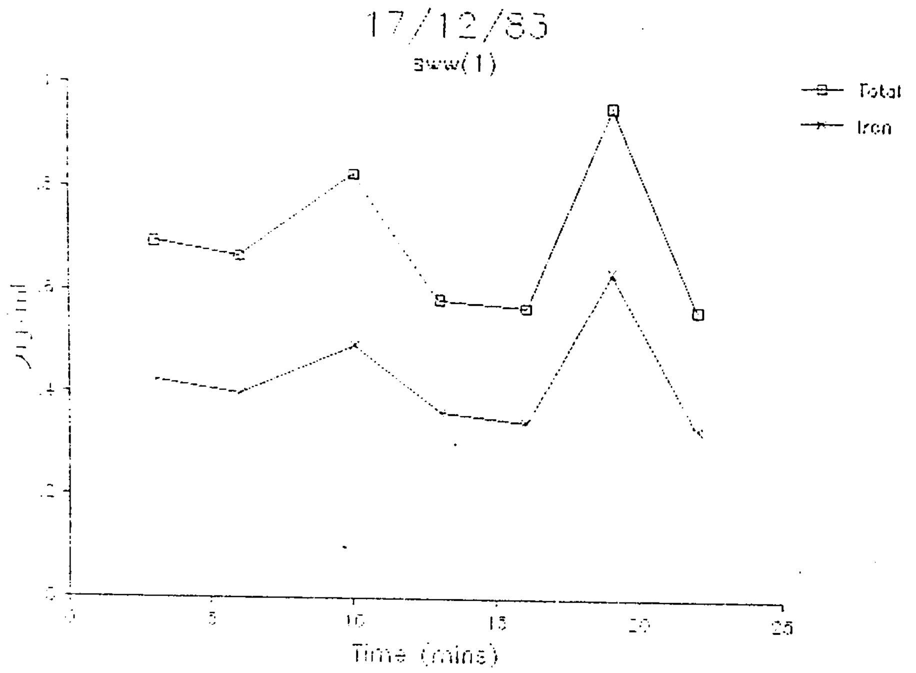
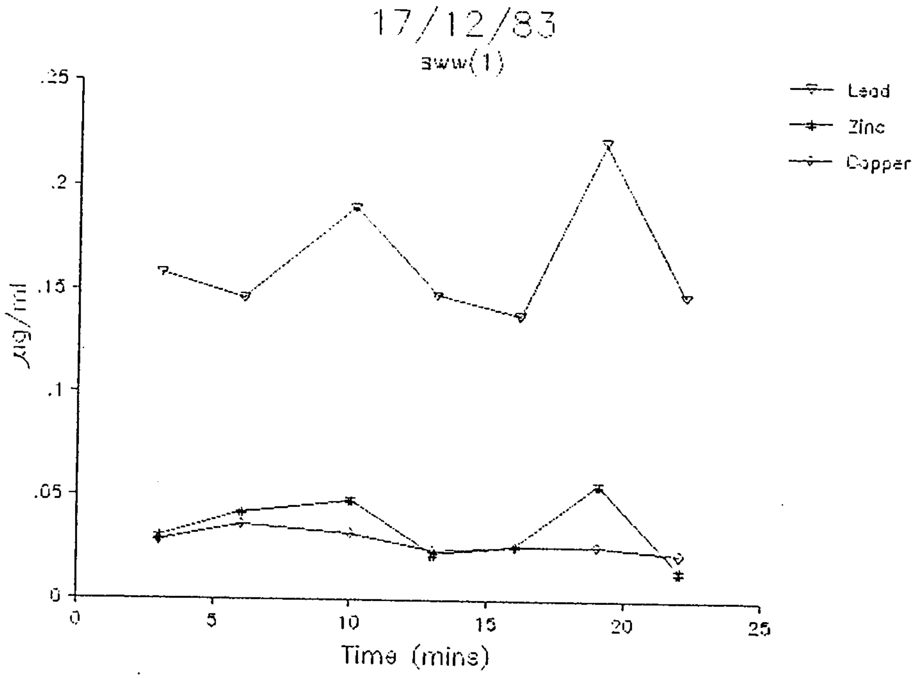


Figure 12.7 Pollutographs for Storm 7.





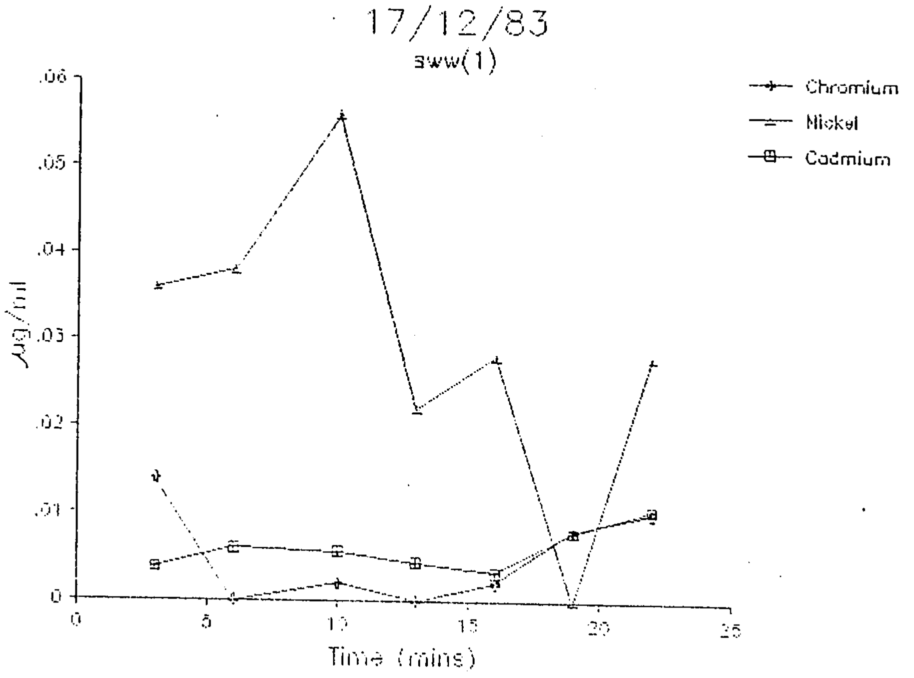
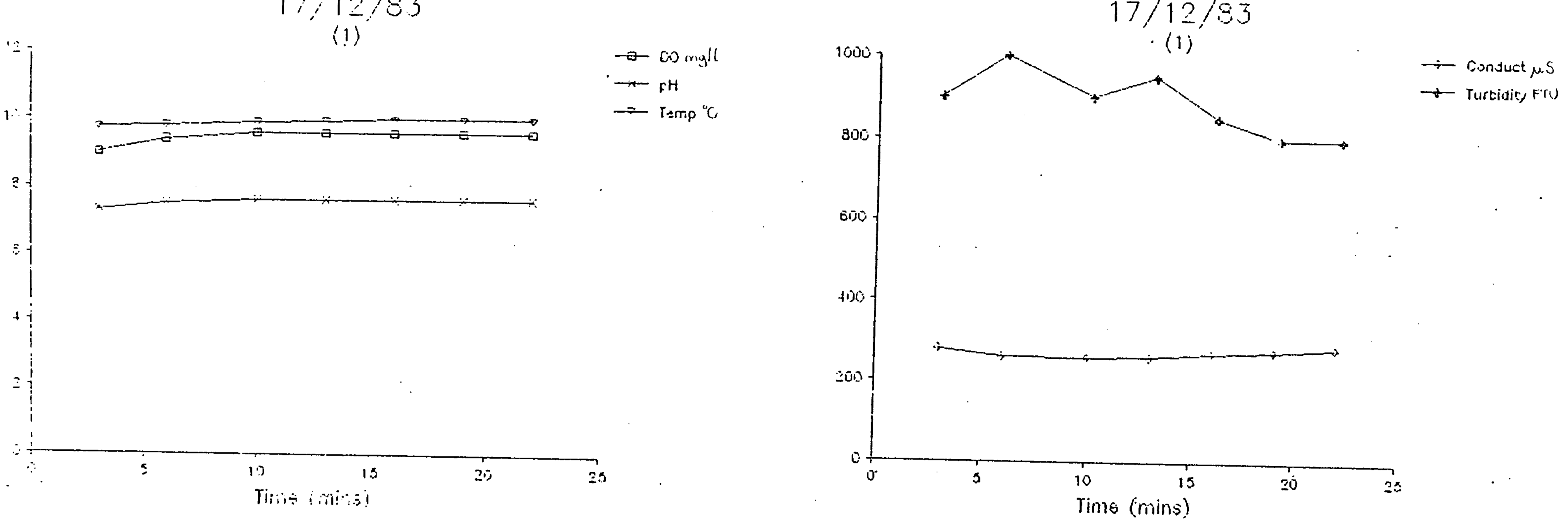


Figure 12.7 cont.



17/12/83 (1)

17/12/83 (1)

Figure 12.7 cont.

The cadmium concentrations were on the increase towards the end of the storm, as was the case with chromium.

Dissolved oxygen concentrations were at their lowest value at the start of the storm, 9 mg/l, and subsequently rose by 0.5 to 9.5 mg/l after 6 minutes, where it then remained for the rest of the storm. After an initial value of 7.3 the pH soon increased to a constant value of 7.6, and the temperature remained constant at 10°C. The conductivity remained roughly constant with the recorded values ranging from 260 to 280 µs. Turbidity was low at the start of the storm and decreased irregularly throughout the event. The values of turbidity displayed an inverse pattern of behaviour to that of conductivity.

12.1.9 Storm 8 (17/12/83) (Figure 12.8)

The flow for storm 8 was characterized by a single wide peak, with flowrates much greater than those experienced during the previous storm of the same day (storm 7). The maximum flowrate of 385 l/sec was attained after 12 minutes.

The particulate metal concentrations displayed no general trend of behaviour. For iron concentration a single peak of 3.56 mg/l was observed after 16 minutes, which coincided with the peak flowrate. Lead concentration attained a peak value of 0.04 mg/l slightly later at a time of 20 minutes. Double peaks, of equal magnitude, were observed for zinc and copper at 10 and 16 minutes respectively with corresponding values of 0.04 and 0.009 mg/l. Chromium concentration also displayed two peaks, the largest one occurring at 16 minutes, 0.017 mg/l, and the smaller one at 10 minutes, 0.015 mg/l. Nickel concentration showed only one peak at 13 minutes, 0.0037 mg/l, whilst

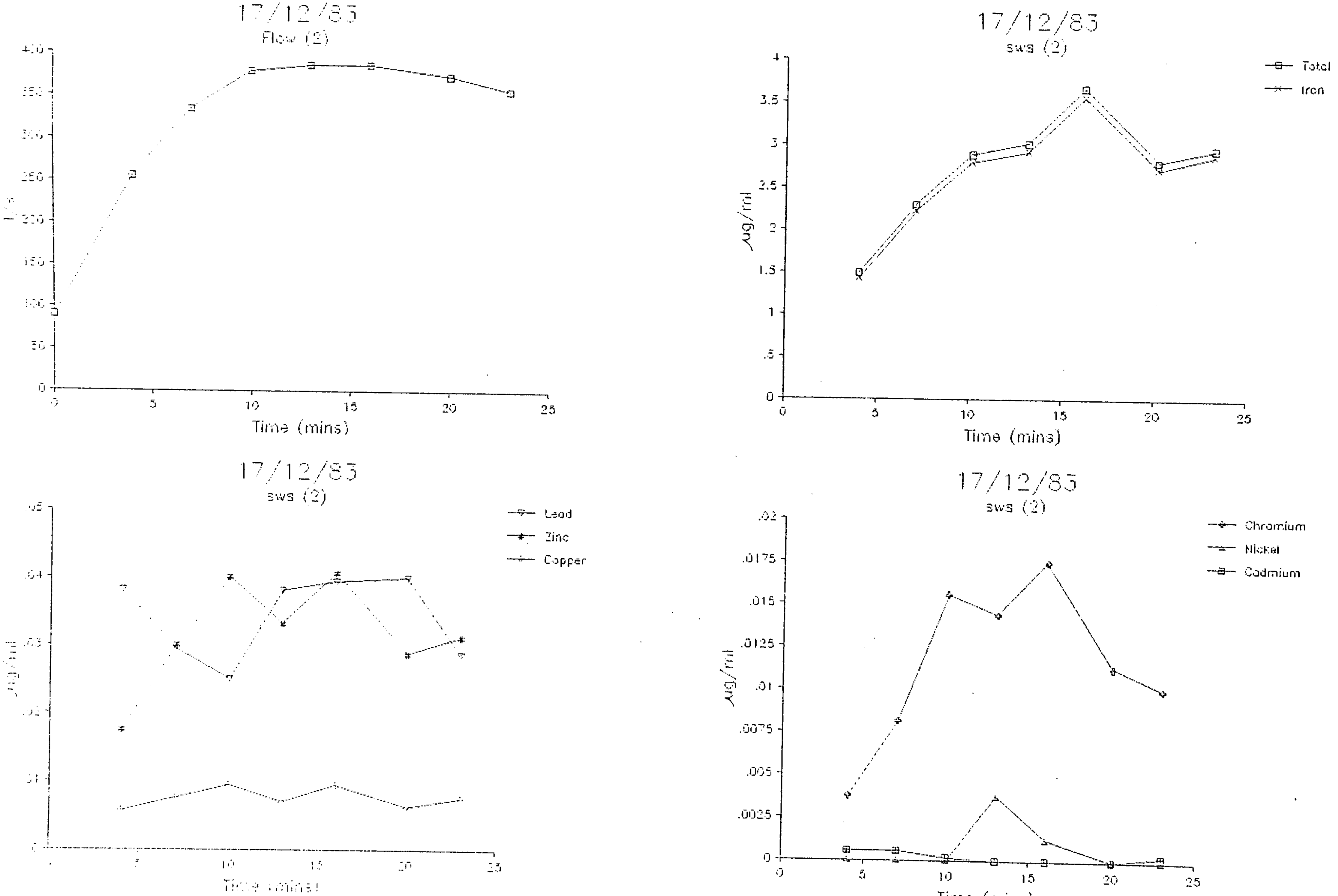
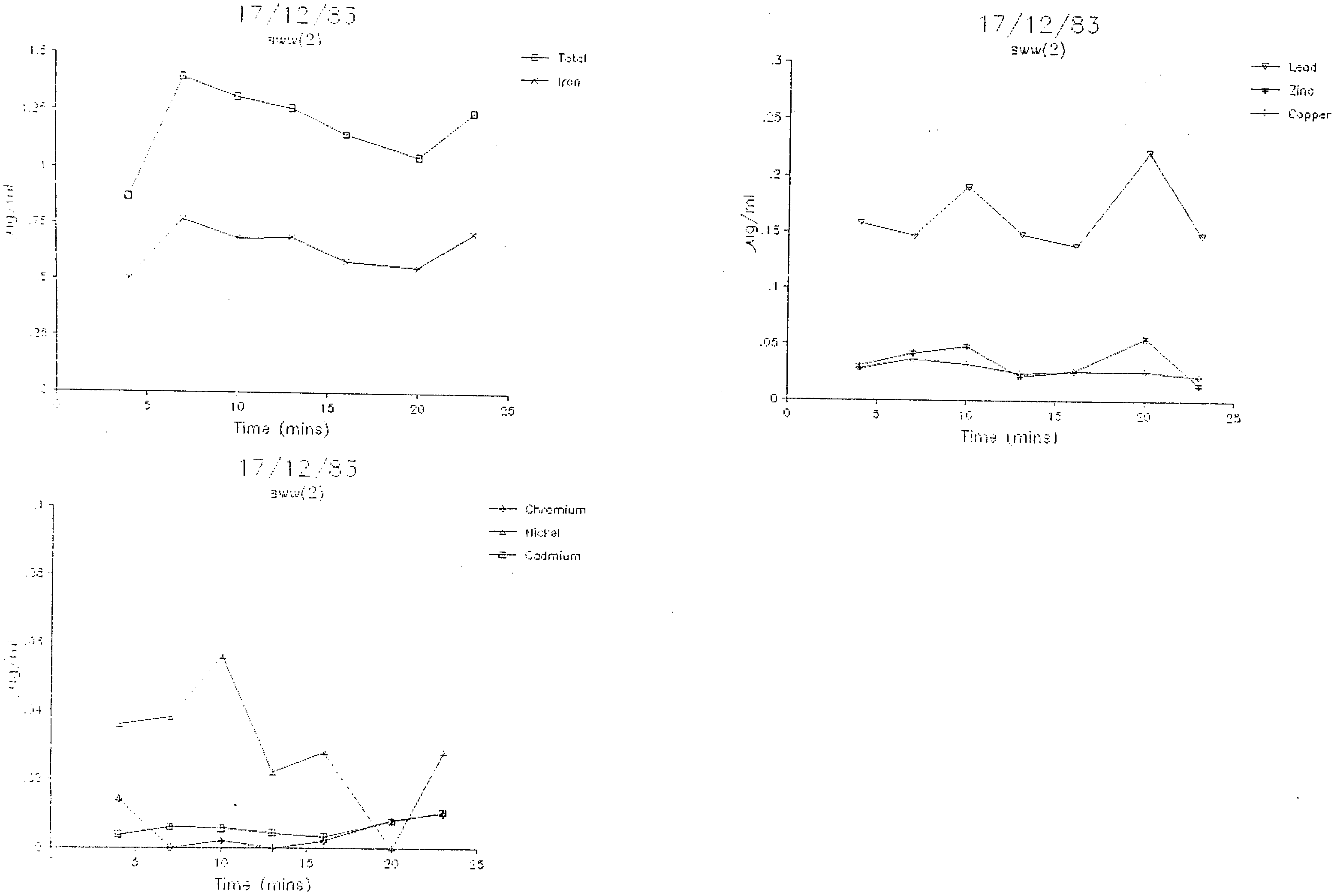


Figure 12.8 Pollutographs for Storm 8.



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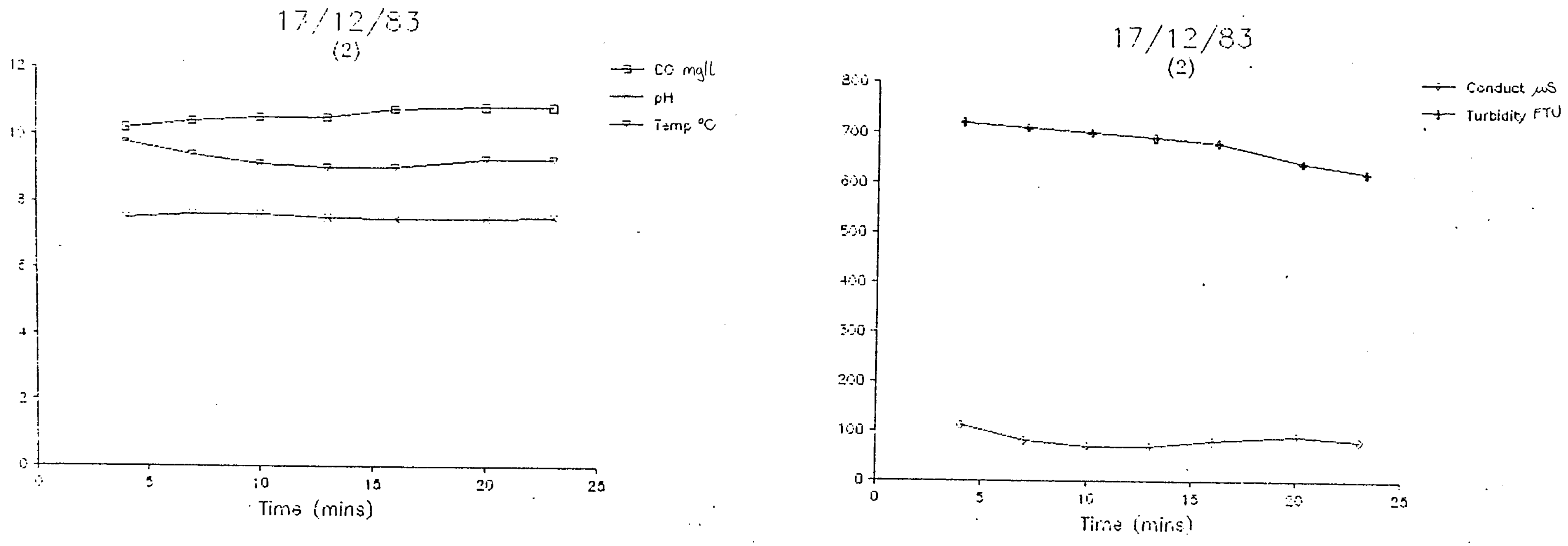


Figure 12.8 cont.

cadmium concentration was highest at the start of the storm, 0.00056 mg/l.

The soluble metal concentrations of lead, zinc and nickel all peaked at a time of 10 minutes, with lead and zinc showing additional later peaks at 20 minutes. Iron concentration displayed an earlier peak of 0.7 mg/l at 7 minutes. Chromium concentrations were highest at both the start and end of the storm, and soluble cadmium concentration appeared to increase once more at the end of the storm.

The dissolved oxygen levels had an initial value of 10.2 mg/l but gradually rose to 10.8 mg/l towards the end of the storm. Both the pH and the temperature remained sensibly constant throughout the storm with values of approximately 7.5 and 9.5°C respectively. The conductivity was slightly higher at the start of the storm, 110 µs, but then decreased to a value of 90 µs after 12 minutes where it remained fairly constant. The turbidity displayed an initial value of 720 FTU but then gradually decreased throughout the storm event to 620 FTU, as with event 7, exhibiting an inverse trend of behaviour to that of conductivity.

12.1.10 Storm 9 (02/01/84) (Figure 12.9)

There was a gradual rise in flowrate where a peak value of 261 l/sec was attained at 98 to 104 minutes, thereafter the flow decreased to a minimum of 188 l/sec at 129 minutes where it then displayed a further increase. Unfortunately only the first part of storm 9 was sampled, the sampler terminated before the end of the storm since it was of a very long duration.

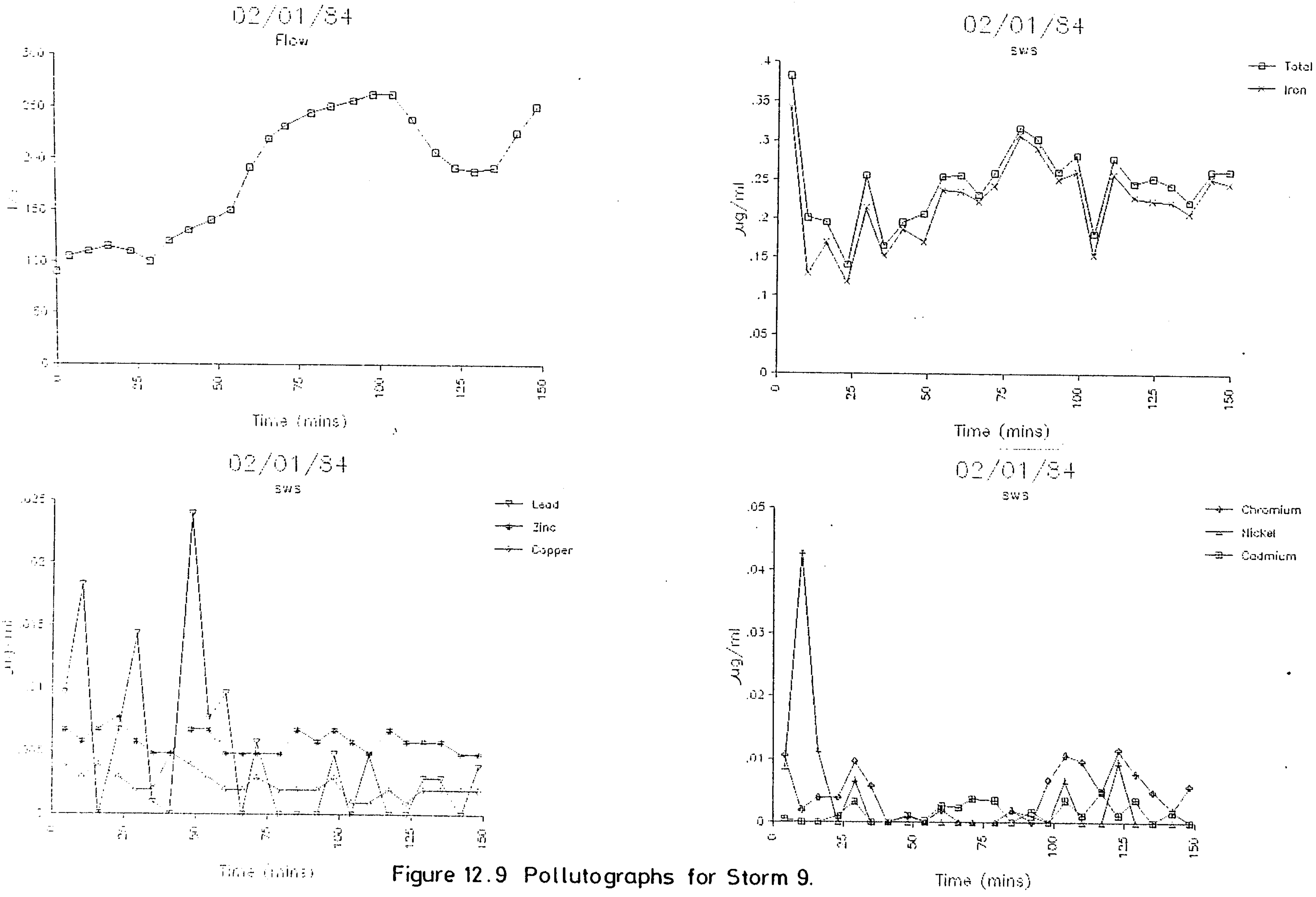
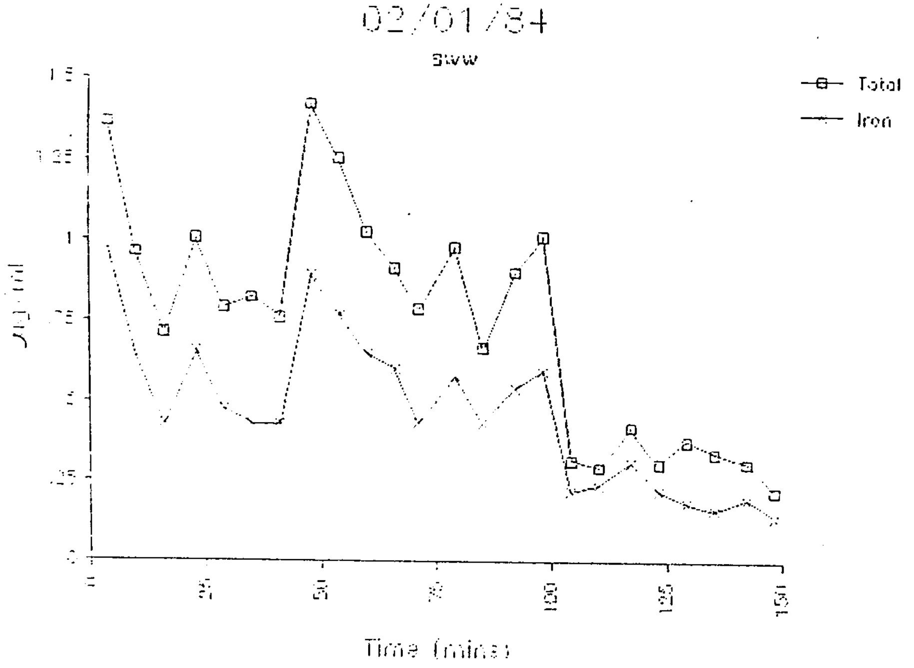
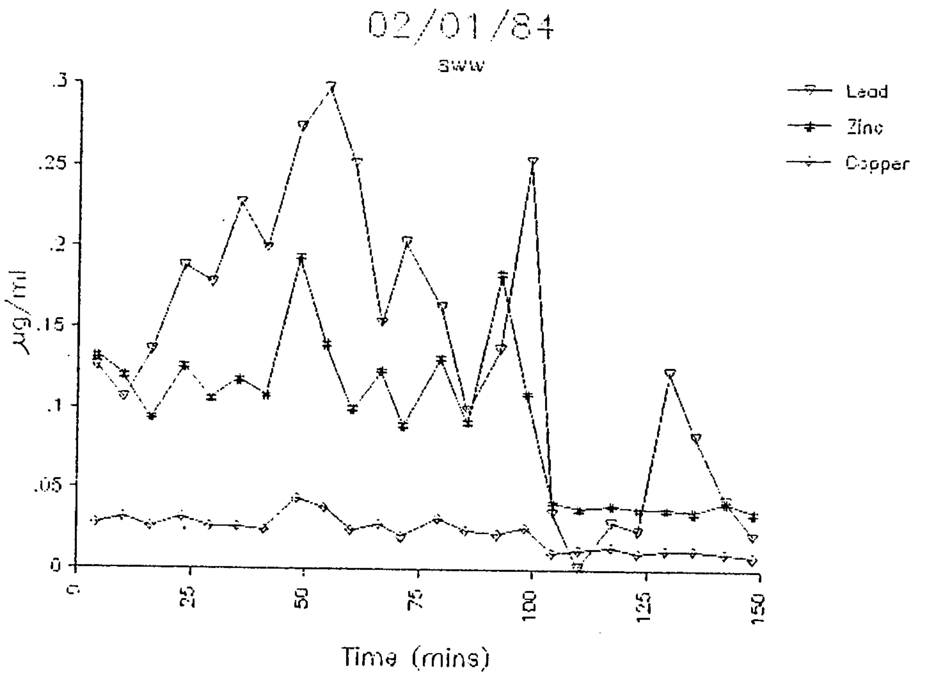
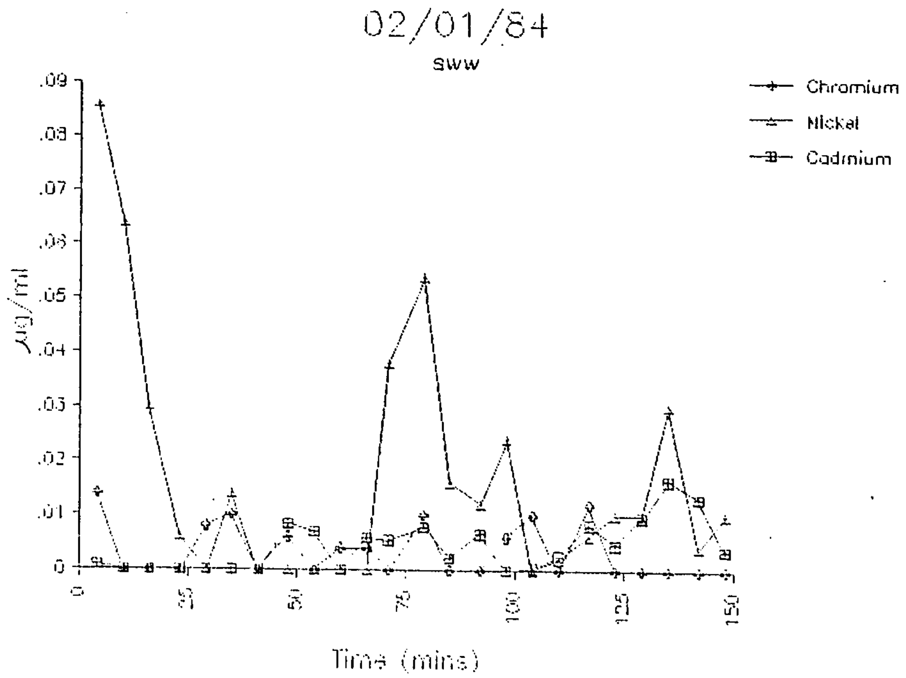


Figure 12.9 Pollutographs for Storm 9.







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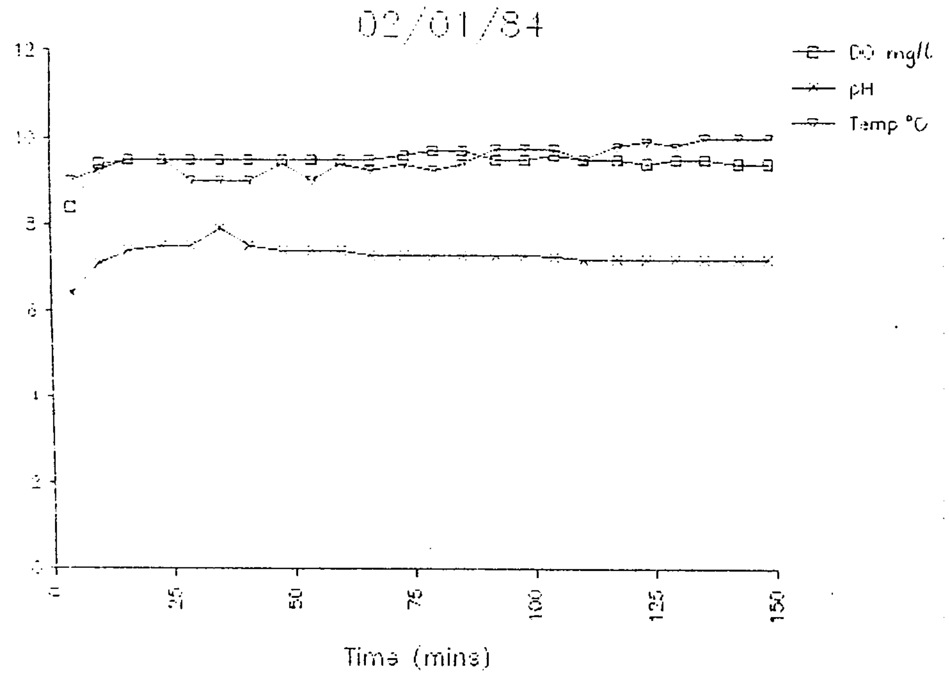
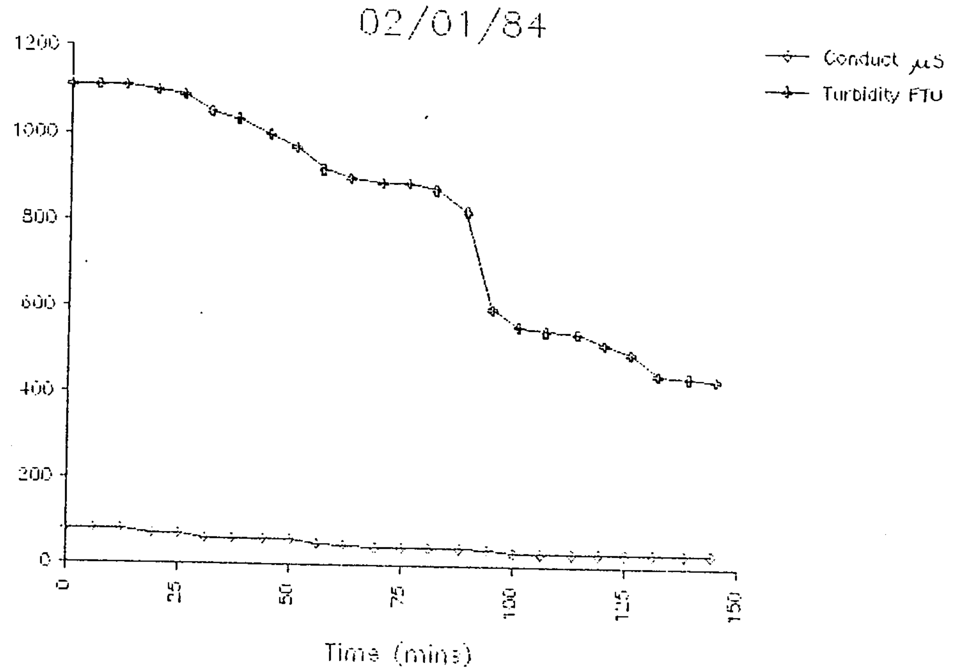
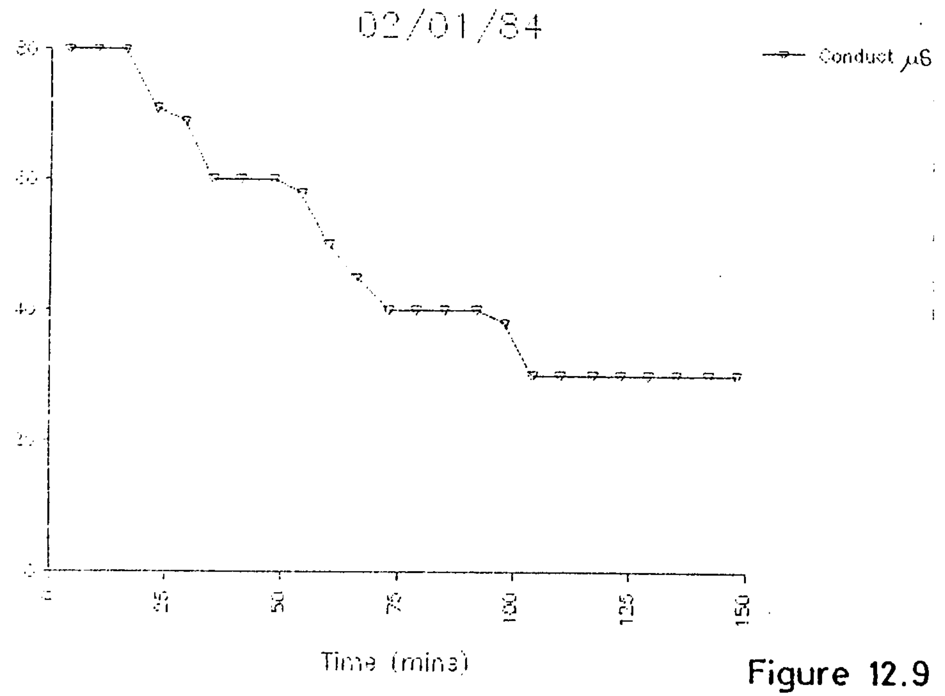






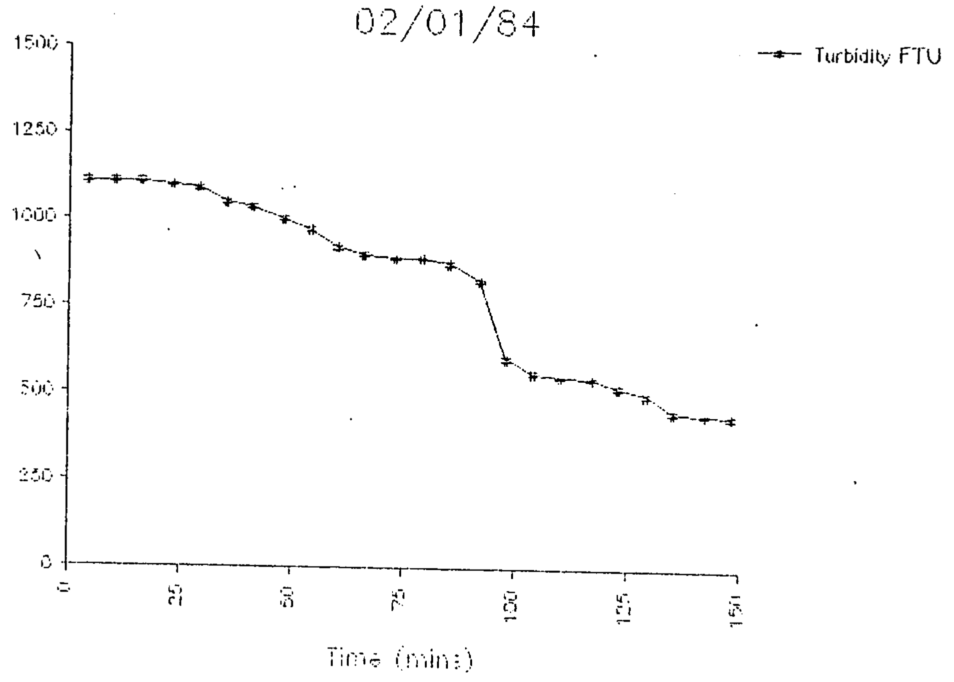


Figure 12.9 cont.

During the event no particular pattern in the particulate metal concentrations could be discerned. Iron, zinc, copper, chromium and cadmium concentration were at their highest at the start of the storm but then fell rapidly within the first few minutes. After the initial decrease in values the metal concentrations tended to fluctuate haphazardly throughout the storm event displaying no distictive pattern. Lead concentration, however, exhibited three large peaks at 10, 29 and 48 minutes, and nickel concentrations peaked at 10 and 29 minutes into the storm as well as an producing additional two peaks at 104 and 123 minutes. Peaking of cadmium concentration was also observed to be irregular and displayed a similar pattern to that of chromium and nickel, the highest value, 0.005 mg/l, occurred towards the end of the storm at a time of 117 minutes.

As was the case for the particulate metal concentrations, the soluble metal concentrations appeared to be rather irregular and appeared to fluctuate randomly. The majority of the metal concentrations (for iron, lead, zinc, chromium and nickel) were highest at the start of the storm and one main peak was evident for most of the metals (including iron, lead, zinc, copper, chromium and cadmium) at 48 to 54 minutes.

Iron concentration attained a peak value of 0.90 mg/l at 48 minutes whilst lead peaked at a value of 0.30 mg/l 54 minutes later. As was the case with iron, zinc and copper peak concentrations of 48 minutes of 0.194 and 0.044 mg/l respectively occurred at 48 minutes. A secondary peak value of 0.184 mg/l at 92 minutes was also observed for zinc. Chromium concentration displayed four fairly uniform peaks of 0.01 mg/l at 35, 79, 104 and 117 minutes, nickel concentration also displayed four peaks at 35, 79, 99 and 135 minutes. The highest cadmium concentrations tended to occur towards the end of the storm where a value of 0.016 mg/l was attained at 135 minutes.

Dissolved oxygen levels were at their lowest at the onset of sampling, with a concentration of 8.4 mg/l, and subsequently increased to 9.4 mg/l after 10 minutes, remaining at this value for the rest of the storm. The values of pH were also at their lowest at the start of the storm but gradually increased to 7.9 after 35 minutes, whilst the temperature gently fluctuated between 9 and 10°C throughout the storm event. The conductivity was at a maximum value at the start of the storm, 80 µs, and then steadily decreased in a stepwise fashion to 30 µs at the end of the storm. The highest turbidity levels recorded were 1100 FTU occurring at the begining of the storm, and gradually decreasing to 825 FTU after 92 minutes. After this turbidity showed a sharp decrease to 600 FTU at 98 minutes and then decreased steadily to 440 FTU at the end of the storm.

12.1.11 Storm 10 (22/01/84) (Figure 12.10)

The runoff event for storm 10 was produced by rainfall/snowmelt, and the runoff hydrograph was characterized by flowrates of less than 150 l/sec for the entire sampling period.

The particulate concentrations for all the metals tended to gradually decrease with time, with the various metals exhibiting different numbers of peaks. Iron, lead, zinc, copper and chromium displayed two distinctive peaks which occurred at 19 and 94 minutes. An additional peak of 0.04 mg/l at 56 minutes was also observed for lead. Chromium displayed two additional peaks, the first at 56 minutes, as with lead, and the second at 131 minutes. Nickel and cadmium concentrations showed a fairly irregular pattern of peaks with

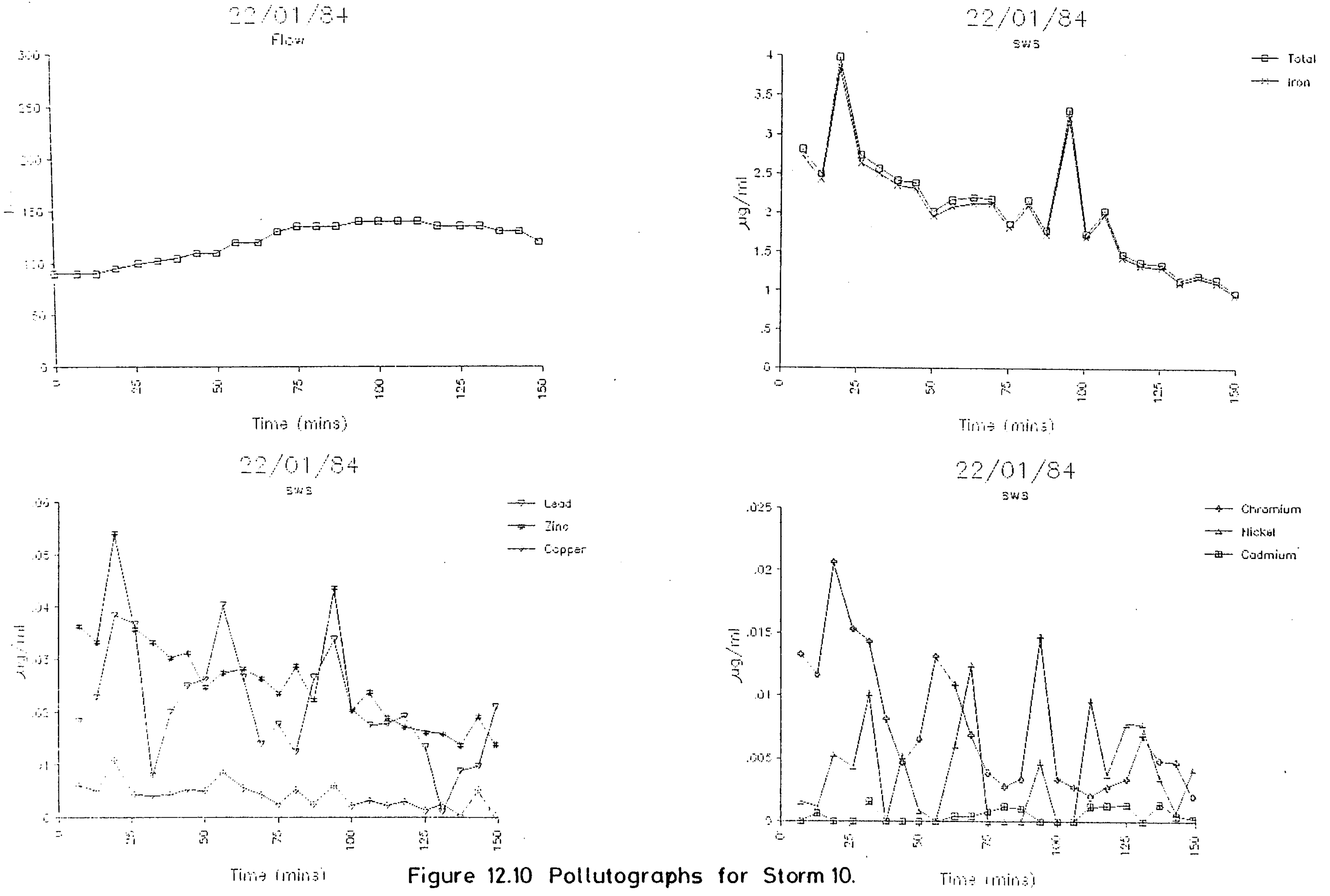
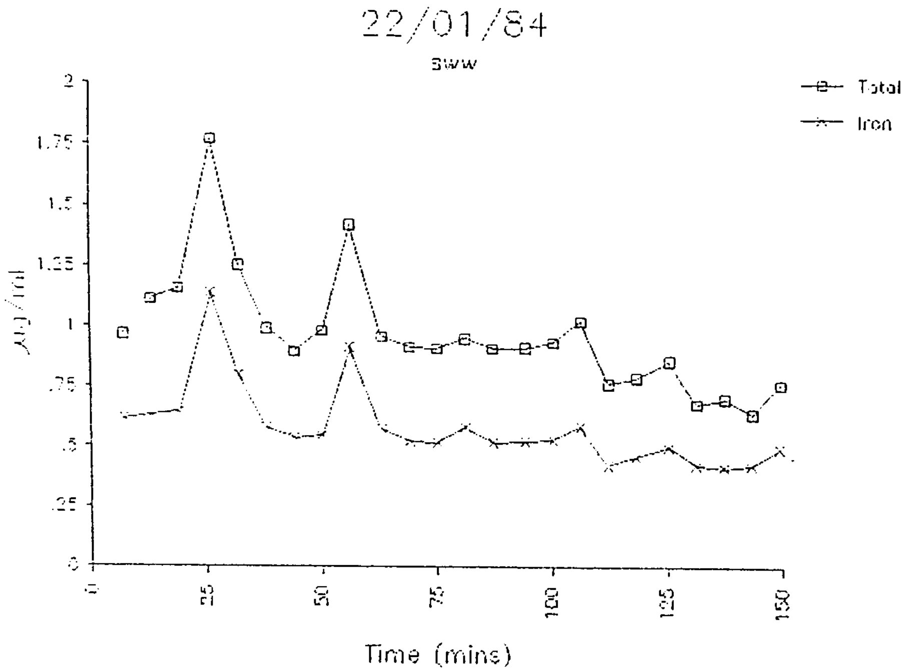
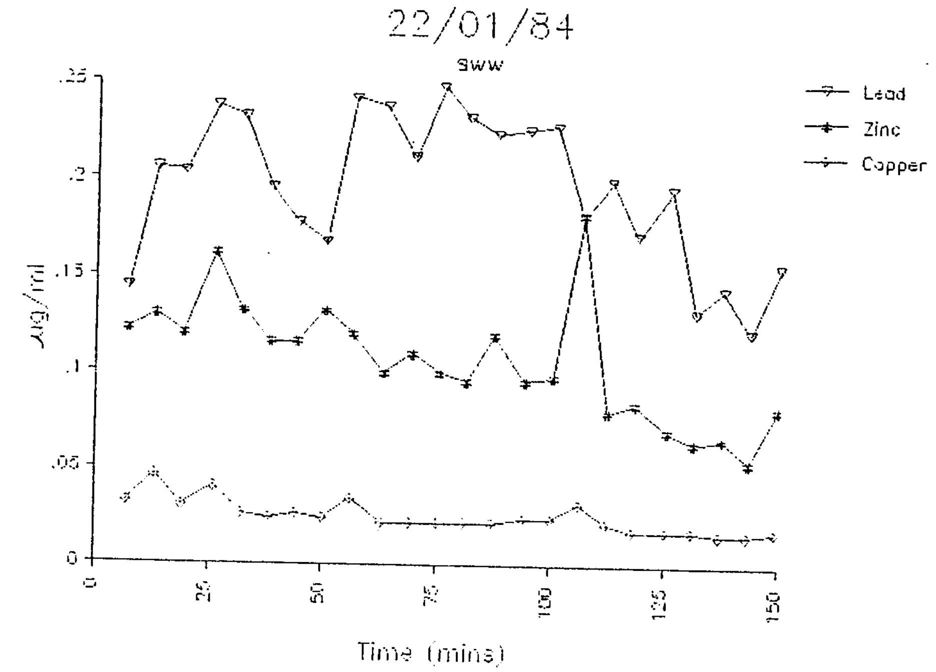


Figure 12.10 Pollutographs for Storm 10.





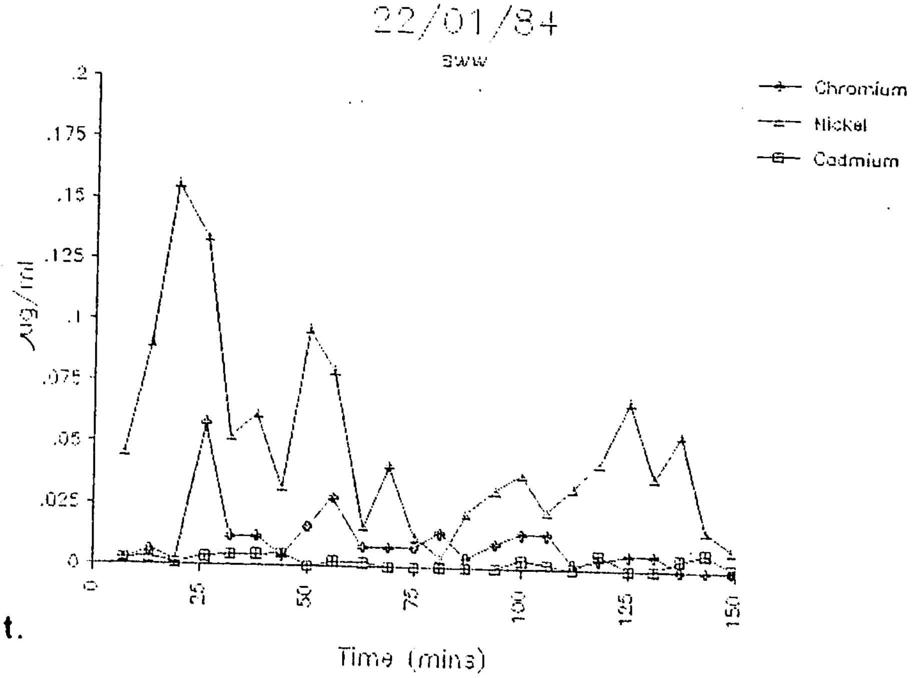


Figure 12.10 cont.

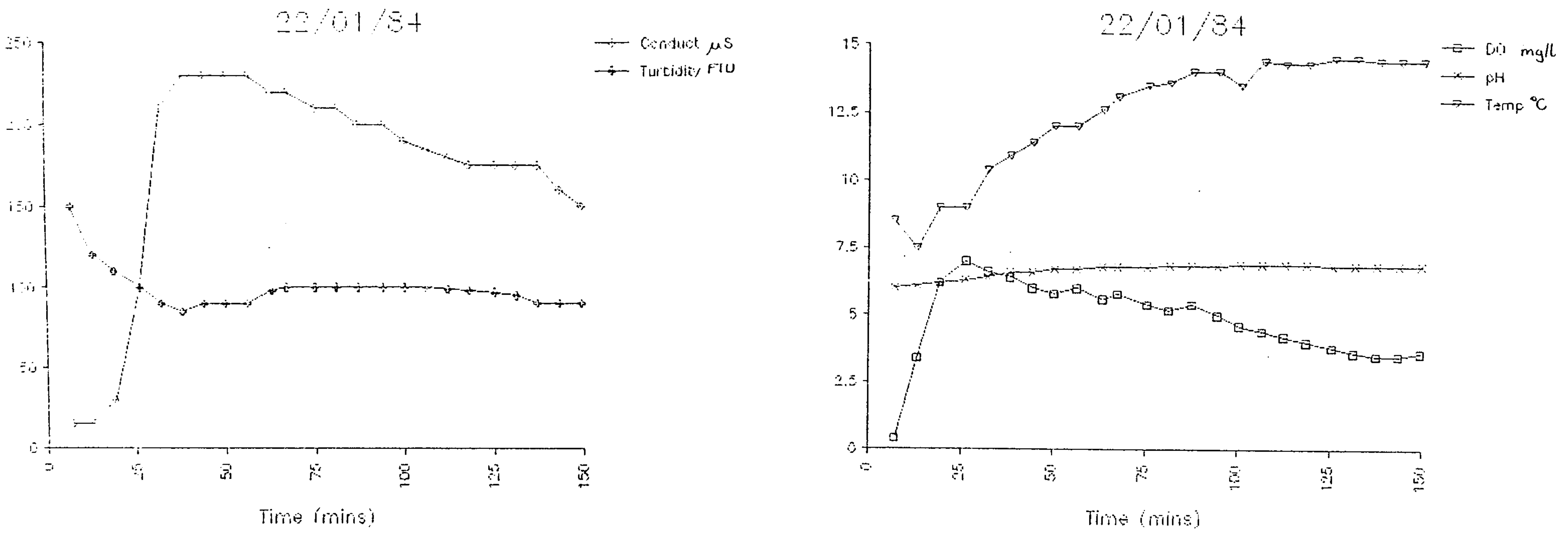


Figure 12.10 cont.

the maximum nickel concentration, 0.0124 mg/l, occurring after 69 minutes and that of cadmium, 0.0016 mg/l, at 32 minutes.

The soluble metal concentration also tended to decrease with time. Two peaks were observed for soluble iron at times of 26 and 56 minutes with corresponding values of 1.136 and 1.42 mg/l respectively. Lead concentrations also displayed peaks at these times with an additional peak, the highest at 0.248 mg/l after 75 minutes. Two main peaks were observed for zinc, 0.162 mg/l at 26 minutes, and 0.182 mg/l at 106 minutes. Copper showed four peaks ranging in value from 0.03 to 0.04 mg/l at 13, 26, 56 and 106 minutes into the storm, the values of concentration between the peaks remained fairly uniform. Chromium also displayed three peaks ranging in value from 0.058 mg/l, at 26 minutes, to 0.014 mg/l, at 81 and 100 minutes. Nickel displayed a similar patern to that of chromium with peaks ranging from 0.156 mg/l at 19 minutes to 0.069 mg/l at 125 minutes. Three peak values of concentration were observed for cadmium at 44, 118 and 143 minutes.

The soluble metal concentrations remained fairly uniform between the slight peaks experienced during the runoff event. This could well be typical of snowmelt, but unfortunately only one such event was encountered during the research sampling period and therefore no general conclusion could be drawn.

The temperature clearly increased throughout the runoff period. The pH remained virtually constant throughout the event at approximately 6.8, showing a slight increase from the start of the runoff. The dissolved oxygen concentration was very low at the start of sampling, 0.4 mg/l, but increased sharply to 7 mg/l at 26 minutes, after which it gradually decreased throughout the remainder of the runoff cycle. Similarly the conductivity increased sharply during the first 30 minutes of runoff to a maximum value of 230 µs, after which it gradually decreased until at the end of the storm it was down to 150 µs. The turbidity displayed an initial high value of 150 FTU but levels decreased fairly rapidly to a minimum of 85 FTU at a time of 38 minutes, thereafter it remained sensibly constant at a value of approximately 90 FTU.

12.1.12 Storm 11 (24/05/84) (Figure 12.11)

Storm 11 displayed the highest recorded flowrates out of all the storms analysed within the sampling period. A peak flowrate of over 2000 l/sec was recorded after only 5 minutes. A second smaller peak with a magnitude of approximately 450 l/sec, was noted after 63 minutes. Since the rise time within the sewer system was very rapid, the sampler missed the first part of the storm. This was reflected by the fact that all of the metal concentrations were high at the start of the sampling cycle.

All of the particulate metal concentrations initially showed very high values which decreased with time, however, some showed slight peaks during the storm. Iron displayed two small late peaks at 71 and 83 minutes and lead was observed to show a slight increase in concentration at 30 minutes. Zinc, copper, chromium, nickel and cadmium concentrations all decreased with time. Cadmium concentration appeared to be on the increase at the end of the storm (0.00137 mg/l) and nickel and chromium concentrations displayed slight increases at 54 and 71 minutes, plus an additional peak for chromium for 0.113 mg/l at 88 minutes.

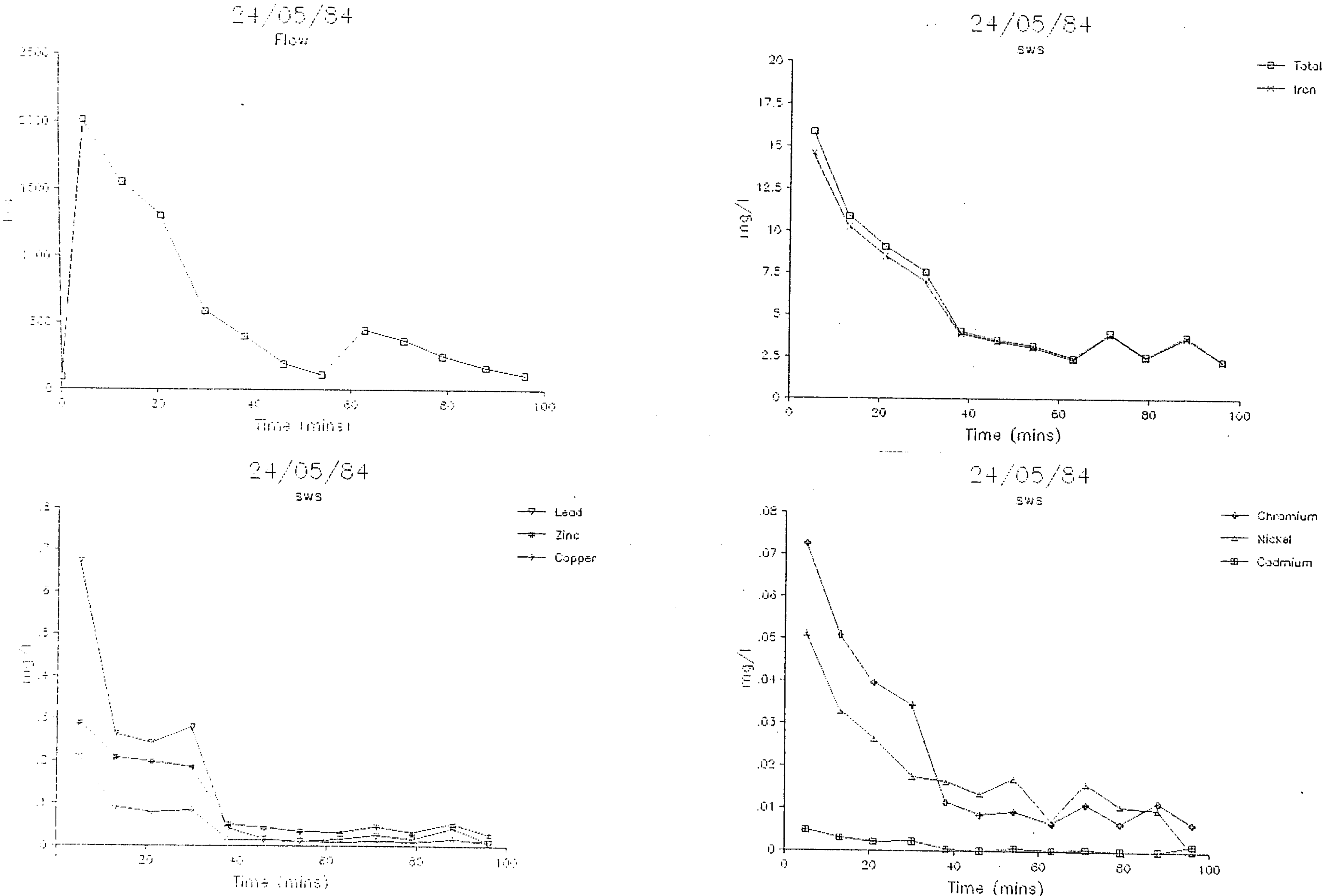


Figure 12.11 Pollutographs for Storm 11.

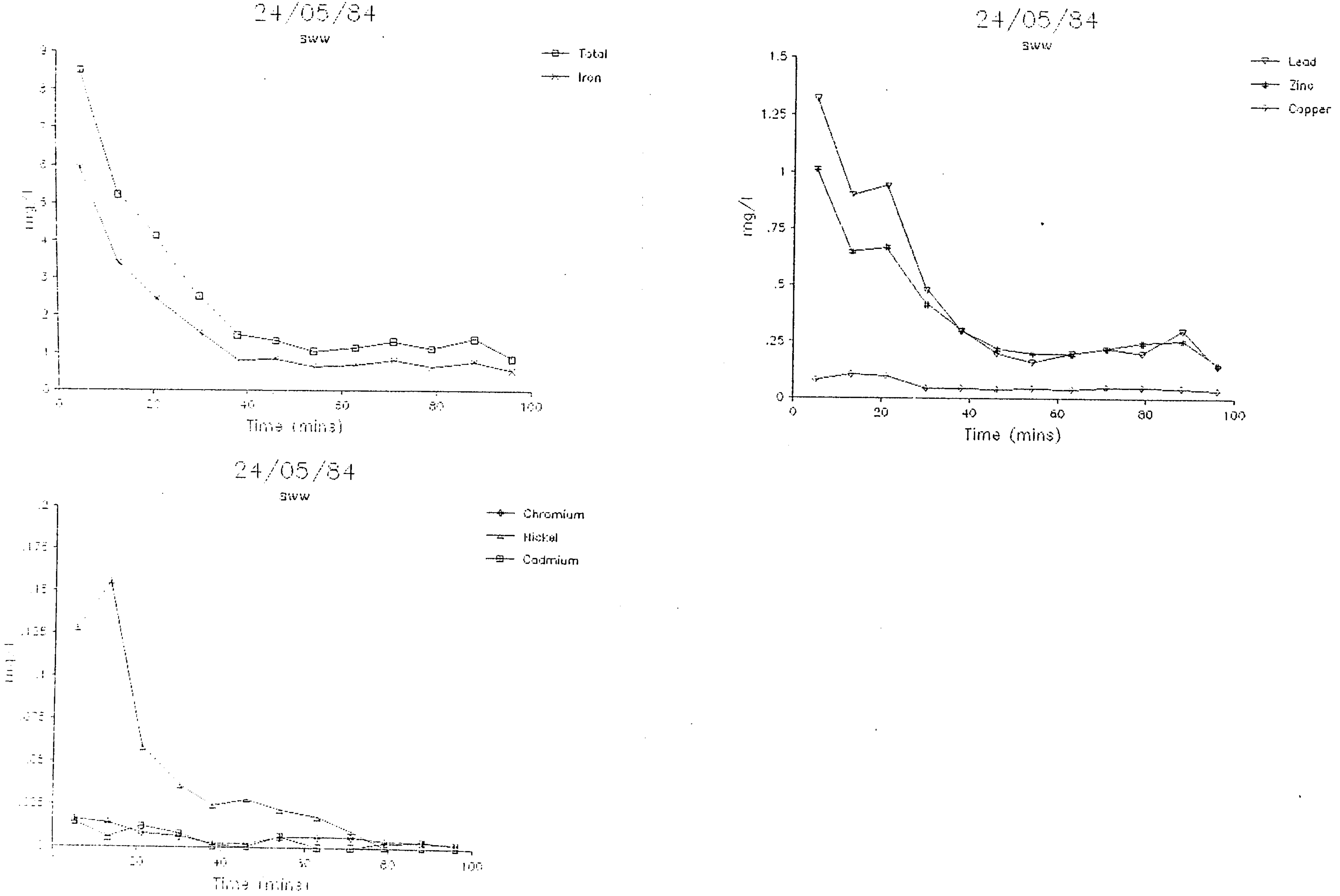


Figure 12.11 cont.

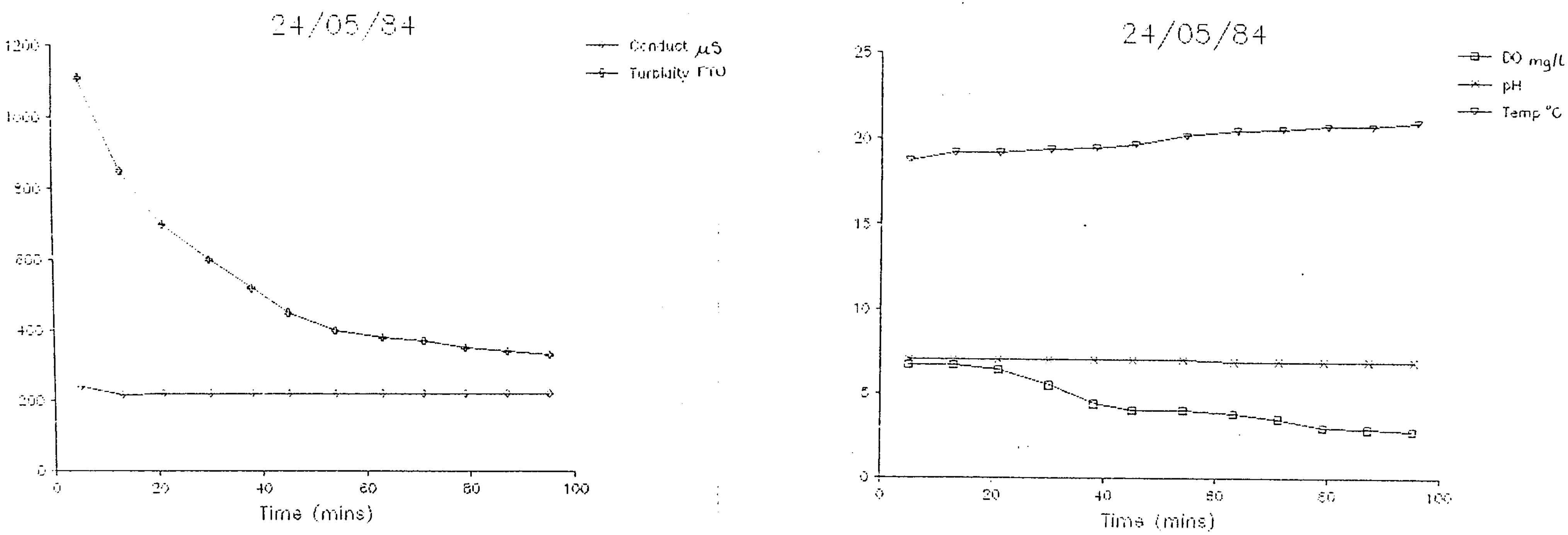


Figure 12.11 cont.

The soluble metal concentrations appeared to follow closely the pattern of behaviour of the particulate metal concentrations throughout the storm event. Initially all metals were fairly high, but subsequently decreased with time, although some of the metals showed slight peaks along the hydrograph. For example, lead peaked at 0.94 mg/l and 0.30 mg/l at 21 and 88 minutes respectively, chromium peaked at 54 minutes with a concentration of 0.006 mg/l, nickel peaked at 13 minutes, 0.16 mg/l, and cadmium at 21 minutes with a value of 0.012 mg/l.

The heavy metal concentrations for storm 11 followed the flowrate closely, whilst displaying a gradual decrease in metal concentrations with decreasing flow. This was possibly due to the large flowrates observed within the catchment which would have allowed most of the pollutants to be removed, and as the storm proceeded the concentrations would tend to decrease due to the effects of progressive scouring (Waller (1972)).

The observed dissolved oxygen levels were highest at the start of the storm (6.7 mg/l), but then gradually decreased throughout the storm to a minimum of 2.8 mg/l. The pH of the stormwater remained constant at approximately 7, but the temperature gradually increased from 19.2 to 21^{o}C. Conductivity exhibited an initial high of 240 μs and then decreased to a value of 220 μs at 21 minutes, where it remained for the rest of the storm. The turbidity values tended to closely follow the flowrate with maximum recorded levels at the start of the storm (1110 FTU) thereafter the turbidity declined in a linear fashion throughout the remainder of the storm, reaching a minimum value of 330 FTU at the end.

12.1.13 Storm 12 (25/05/84) (Figure 12.12)

The peak flow for storm 12 was attained after 49 minutes with a magnitude of 260 l/sec.

No general trend was evident for any of the particulate metal concentrations, but most metals displayed two slight peaks however these were at different times. There was, however, a general decrease in concentration with time. Iron concentration showed one major peak at 33 minutes with a value of 0.645 mg/l, plus a smaller peak of 0.376 mg/l 74 minutes into the storm period. The concentration of lead peaked at the start of the sampling cycle and then decreased to zero for the rest of the storm. Zinc concentrations displayed one large late peak of 0.0072 mg/l, at 74 minutes, plus a smaller earlier peak of 0.0056 mg/l at 49 minutes. Three equal peaks of 0.24 mg/l at 9, 33 and 66 minutes were observed for copper, but chromium, nickel and cadmium all displayed two peaks but at various times.

Although no distinct pattern could be observed for the soluble metal concentrations, there was an overall decrease in levels with time. Iron concentrations displayed this gradual decrease, lead levels increased at the end of the storm whilst zinc showed a large peak of 0.4 mg/l after 9 minutes. The concentration of copper remained fairly constant throughout the bulk of the storm, but rose rapidly at the end. Chromium displayed two late peaks of 0.008 mg/l at 57 minutes and 0.006 mg/l at 74 minutes. Nickel concentrations were initially at their highest, but after a period of decrease displayed a later peak of 0.03 mg/l at 57 minutes. Cadmium displayed both an early peak of 0.004 mg/l after 9 minutes and a later peak of 0.005 mg/l after 66 minutes.

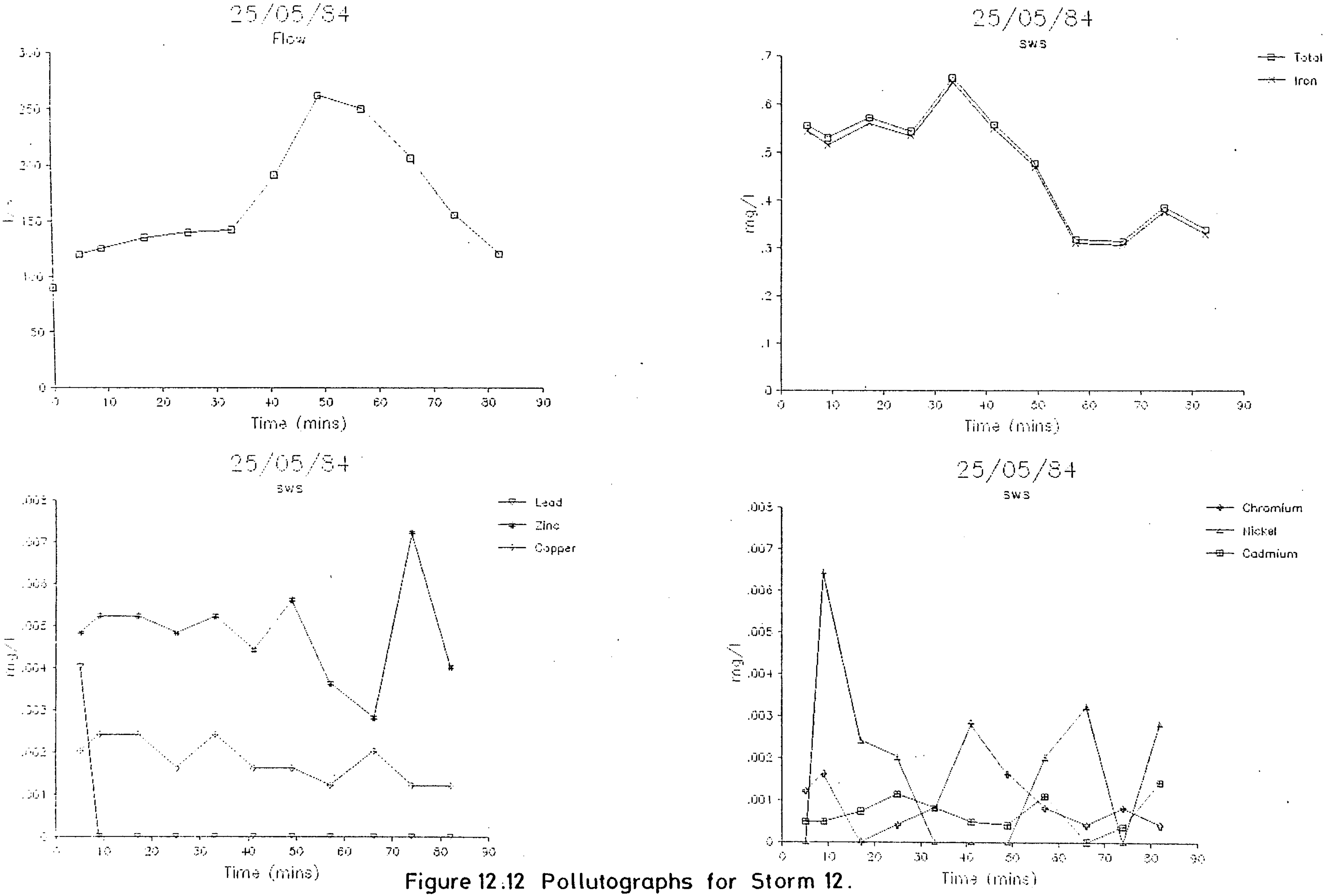


Figure 12.12 Pollutographs for Storm 12.

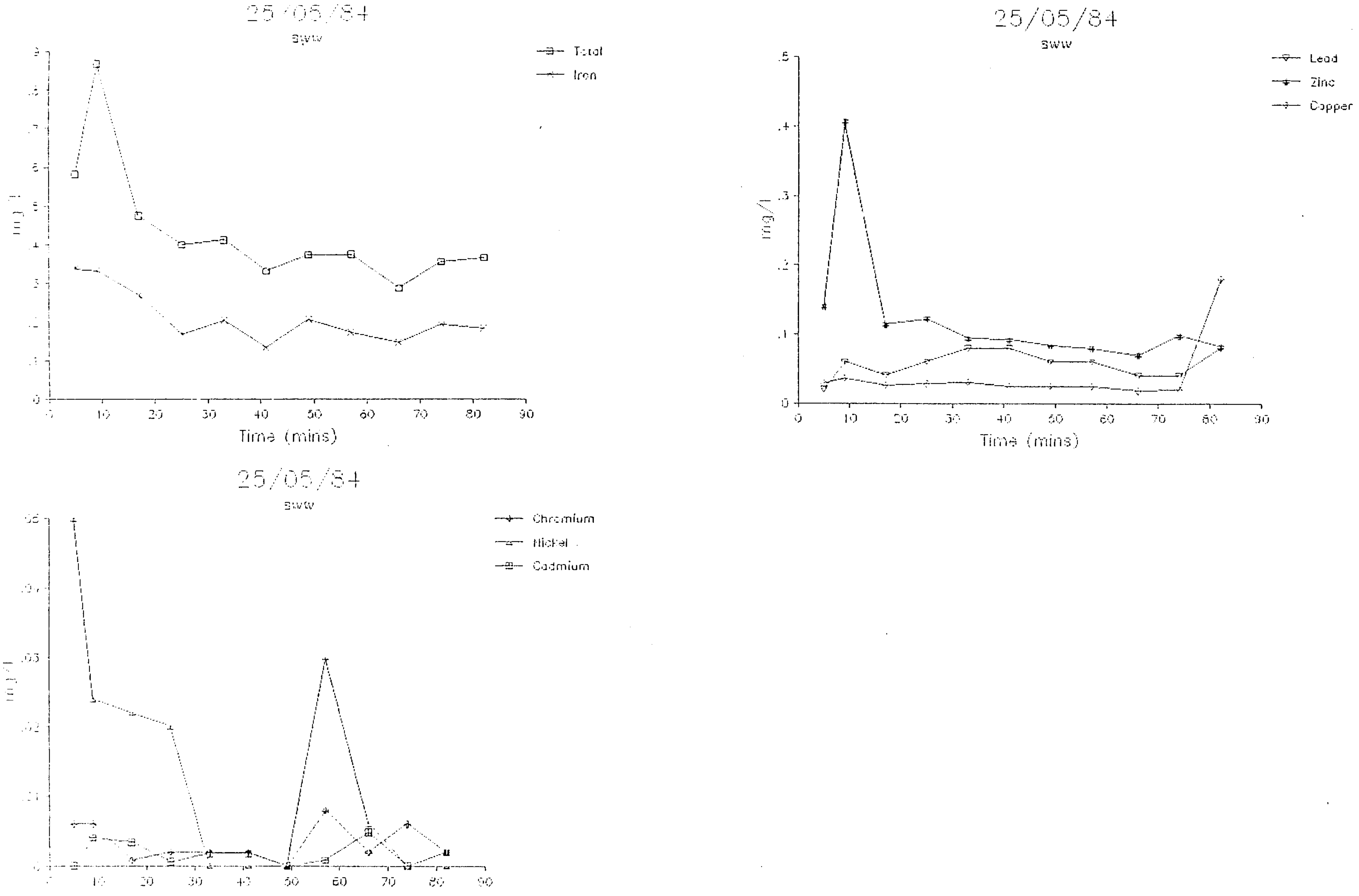


Figure 12.12 cont.

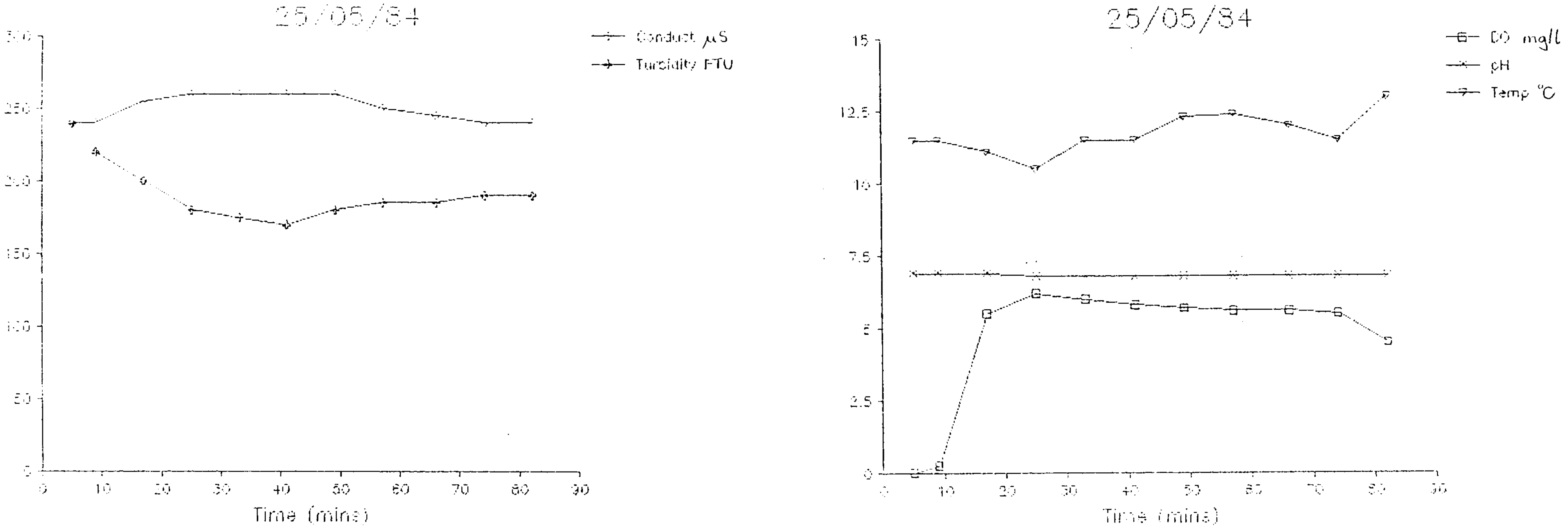


Figure 12.12 cont.

The dissolved oxygen concentrations rose from an initial value of zero to a maximum value of 6.2 mg/l at 25 minutes and thereafter gradually decreased throughout the remainder of the storm. Values of pH remained sensibly constant throughout the entire storm with a value of approximately 6.8. The temperature fluctuated between 10.5 and 13^{o}C throughout the storm, but generally showed a gradual increase. Conductivity levels remained reasonably constant throughout the storm but slightly lower levels (240 μs) were displayed both at the beginning and end of the storm period. Turbidity was highest at the start of the sampling cycle, with a value of 240 FTU, but decreased to a minimum of 170 FTU at 41 minutes, and thereafter it rose to 190 FTU towards the end of the storm. Turbidity yet again showed an inverse relationship to that of conductivity.

12.1.14 Storm 13 (20/06/84) (Figure 12.13)

The flowrates throughout the duration of storm 13 remained relatively low with the maximum value of 200 l/sec occurring at the start of the event. Thereafter the flow gradually decreased, although a slight increase to 120 l/sec was noted at 13 minutes into the storm.

All of the particulate metal concentrations were initially low but increased towards the end of the sampling period. In most cases the metals displayed a rapid increase followed by a slight decrease at 13 minutes, and after 20 minutes all of the metals had begun to rise once more. Iron, copper and chromium concentrations peaked twice at 13 and 24 minutes. Lead maintained a steady increase throughout the storm but displayed a rapid rise at the end. Zinc and nickel concentrations showed earlier peaks at 9 minutes with values of 0.078 and 0.015 mg/l respectively. Cadmium concentration also displayed a peak of 0.007 mg/l at 13 minutes.

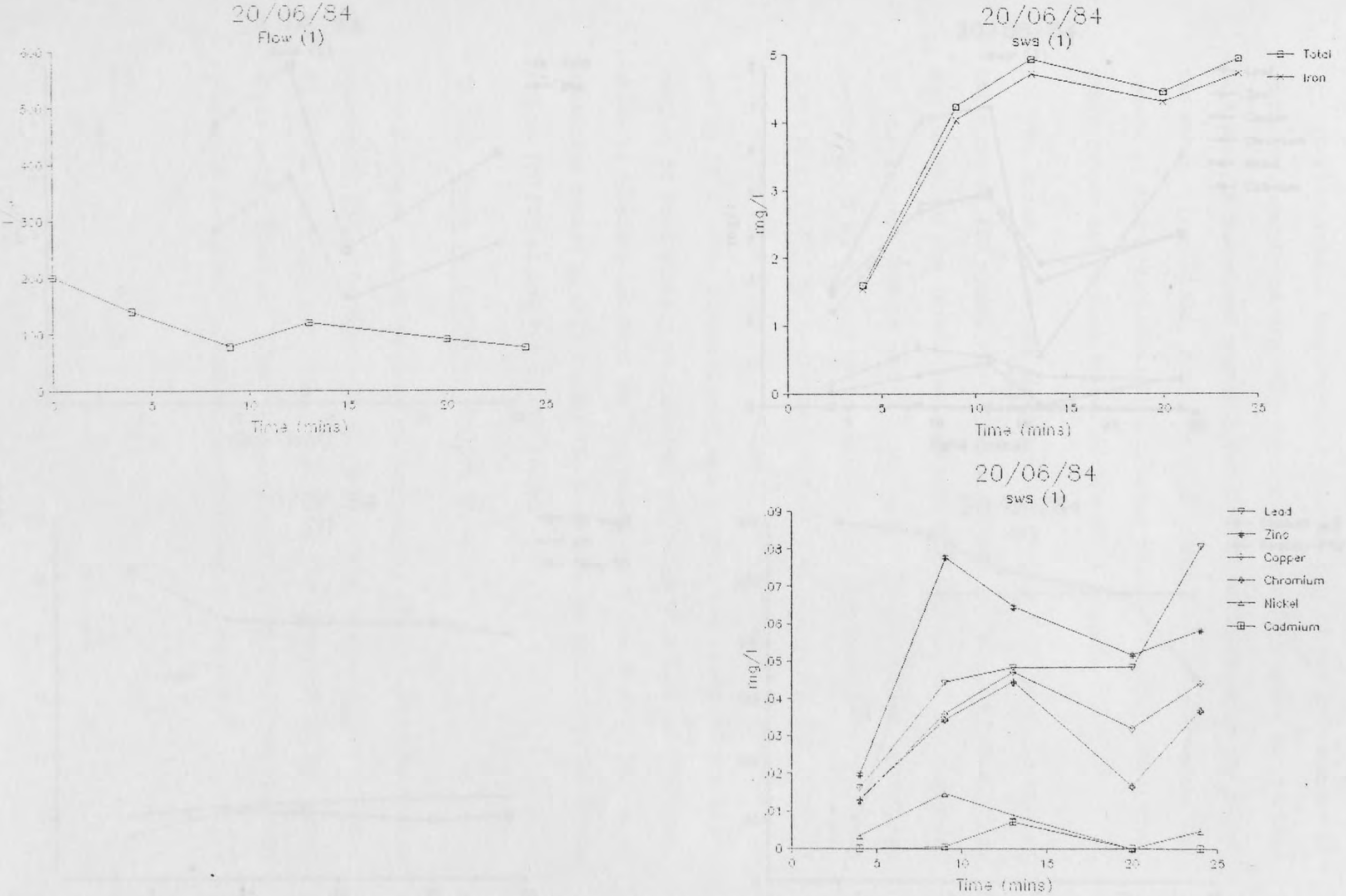


Figure 12.13 Pollutographs for Storm 13.

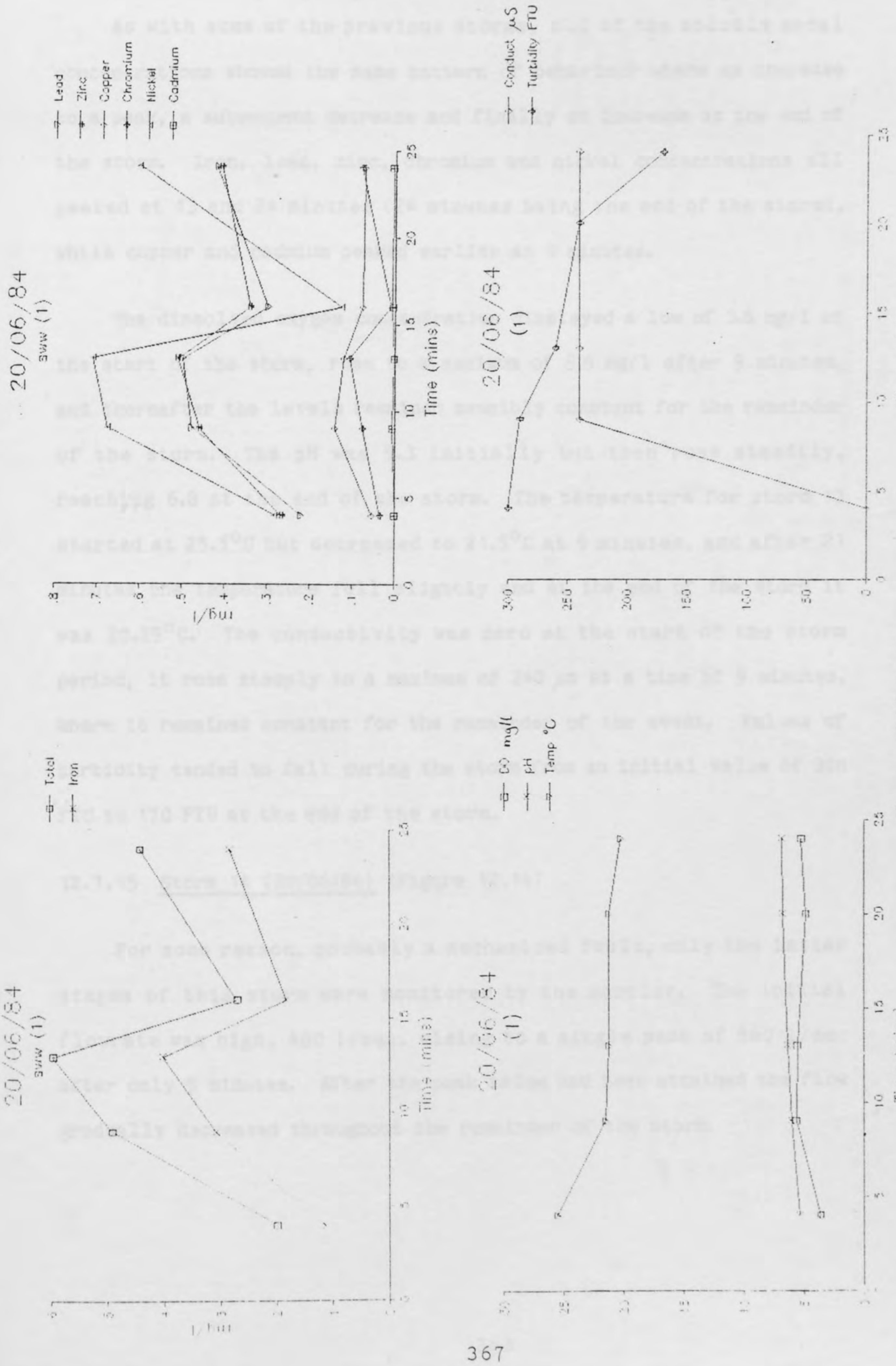


Figure 12.13 cont.

As with some of the previous storms, all of the soluble metal concentrations showed the same pattern of behaviour where an increase to a peak, a subsequent decrease and finally an increase at the end of the storm. Iron, lead, zinc, chromium and nickel concentrations all peaked at 13 and 24 minutes (24 minutes being the end of the storm), while copper and cadmium peaked earlier at 9 minutes.

The dissolved oxygen concentration displayed a low of 3.6 mg/l at the start of the storm, rose to a maximum of 5.6 mg/l after 9 minutes, and thereafter the levels remained sensibly constant for the remainder of the storm. The pH was 5.3 initially but then rose steadily, reaching 6.8 at the end of the storm. The temperature for storm 13 started at 25.5°C but decreased to 21.5°C at 9 minutes, and after 21 minutes the temperature fell slightly and at the end of the storm it was 20.25°C. The conductivity was zero at the start of the storm period, it rose steeply to a maximum of 240 μs at a time of 9 minutes, where it remained constant for the remainder of the event. Values of turbidity tended to fall during the storm from an initial value of 300 FTU to 170 FTU at the end of the storm.

12.1.15 Storm 14 (20/06/84) (Figure 12.14)

For some reason, probably a mechanical fault, only the latter stages of this storm were monitored by the sampler. The initial flowrate was high, 400 l/sec, rising to a single peak of 560 l/sec after only 5 minutes. After the peak value had been attained the flow gradually decreased throughout the remainder of the storm.

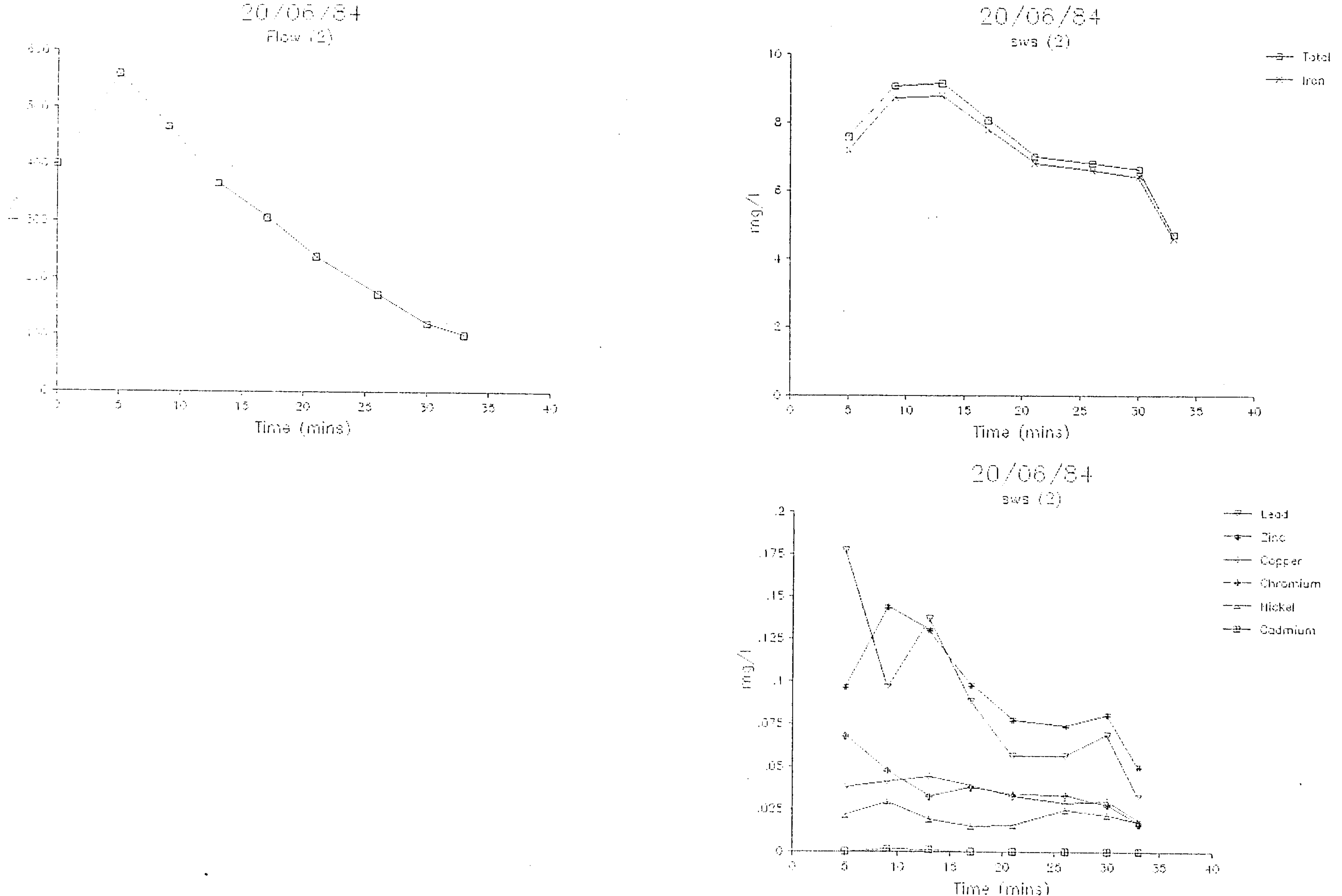


Figure 12.14 Pollutographs for Storm 14.

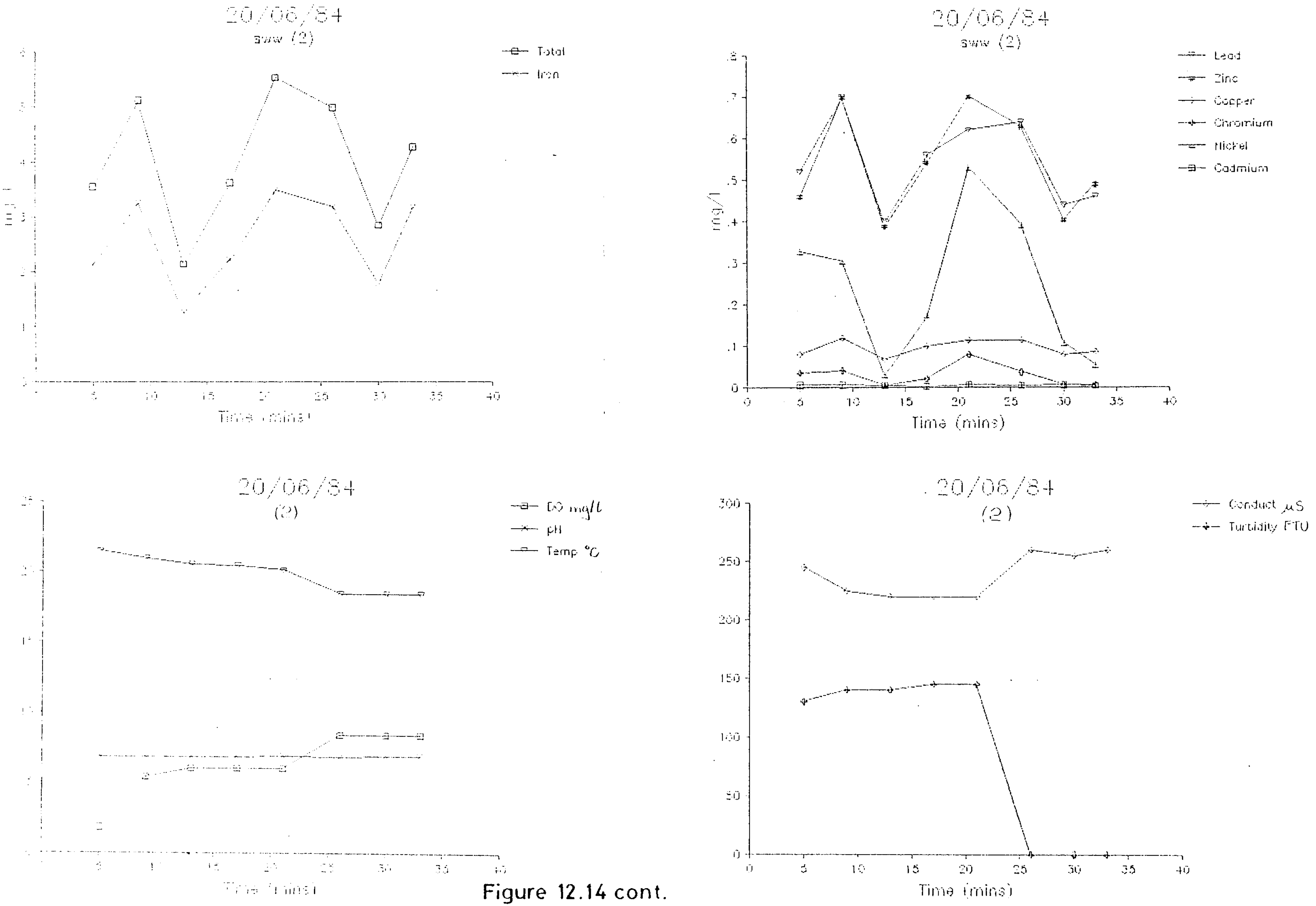


Figure 12.14 cont.

As the sampler only started operating part way through the storm, generally only a fall in particulate metal concentration was observed with time, although some metals displayed slight peaks. The concentration of iron showed a slight peak of 8.8 mg/l between 9 and 13 minutes. The concentration of lead also displayed a peak of 0.137 mg/l at 13 minutes with a further increase to 0.07 mg/l at 30 minutes. The primary peak in zinc concentration was observed before that of lead, i.e. before 9 minutes, whilst a later smaller secondary peak coincided with that of lead, i.e. at 30 minutes. Copper displayed a peak after 13 minutes and cadmium after 9 minutes. Chromium concentrations were initially high, as with lead, and nickel concentrations displayed an undulating trend with two peaks of 0.03 and 0.02 mg/l at 9 minutes and 26 minutes respectively.

It was observed that all of the soluble metal concentrations displayed a peak in value 9 minutes into the storm period, thereafter the concentrations decreased, some very rapidly (e.g. iron, lead, zinc and nickel), subsequently increasing to a second peak between 21 and 26 minutes. For all of the soluble metal concentrations, except that for nickel, an initial low was displayed which then increased during the first flush. Further, all the metal concentrations, again apart from nickel, displayed an increase towards the end of the storm.

The dissolved oxygen concentration displayed a steady increase in value throughout the duration of the storm from 1.8 to 8.4 mg/l. The pH remained sensibly constant at 6.8 whilst the temperature gradually decreased with time from 21.5^{o}C to 18.5^{o}C. Values of conductivity for storm 14 gradually decreased from the start of the storm to a minimum of 220 μs at 15 minutes, thereafter the conductivity increased and reached 260 μs at the end of the storm. Turbidity was effectively constant for the first 20 minutes of the storm, thereafter a sharp drop occurred until it became zero at 21 minutes, where it stayed for the remainder of the storm.

12.1.16 Storm 15 (15/07/84) (Figure 12.15)

Storm 15 was of short length lasting only 28 minutes. Two small peaks in flowrate were recorded at 4 and 16 minutes, with values of 200 l/sec and 190 l/sec respectively.

In most instances a decrease in particulate metal concentration with time was observed. The initial values of lead, zinc, copper and cadmium concentrations were high but subsequently decreased with time. However, iron, nickel and chromium displayed slightly lower values of concentration in the initial stages of the storm, subsequently they increased and then decreased within the first few minutes of the storm. By the end of the event zinc, copper and chromium had remained constant for some time, whilst iron, nickel and cadmium had increased in value and lead had decreased. Iron, chromium and nickel displayed peak values of 3.69, 0.016 and 0.011 mg/l respectively at a time of 48 minutes. Chromium and lead also showed an earlier peak at 20 minutes. The maximum concentrations of cadmium occurred at the start of the storm and at a peak of 0.001 mg/l after 20 minutes.

As with the particulate metal concentrations, the soluble metal concentrations generally decreased with storm duration. Iron, copper and nickel concentrations displayed peaks after 16 minutes, whilst nickel peaked earlier with a maximum of 0.104 mg/l at a time of 8 minutes. The lead concentration showed a peak of 0.10 mg/l at 12 minutes whilst zinc and chromium peaked later at 24 minutes. The cadmium had an initial high value of 0.0032 mg/l and a peak of 0.0046

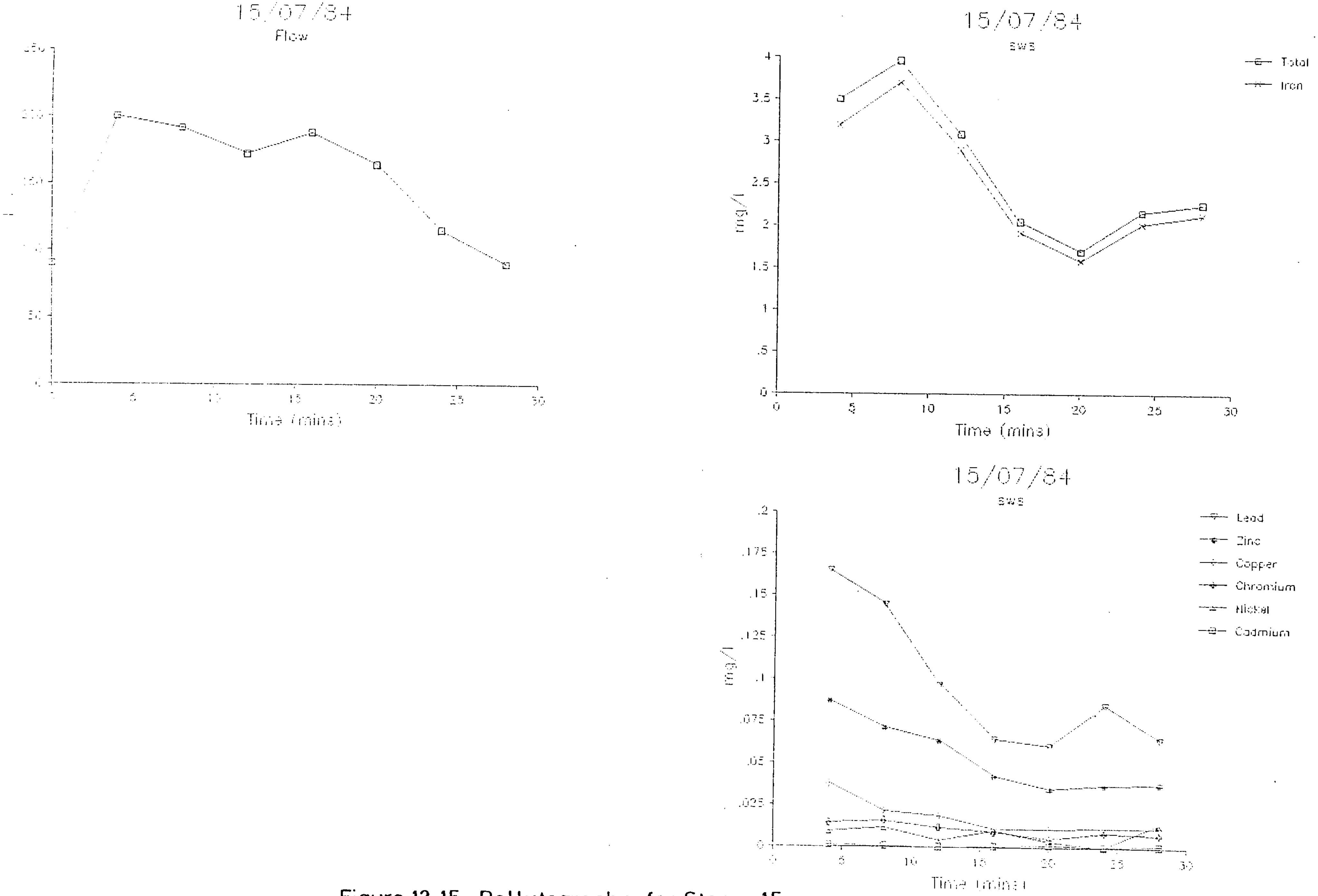


Figure 12.15 Pollutographs for Storm 15.

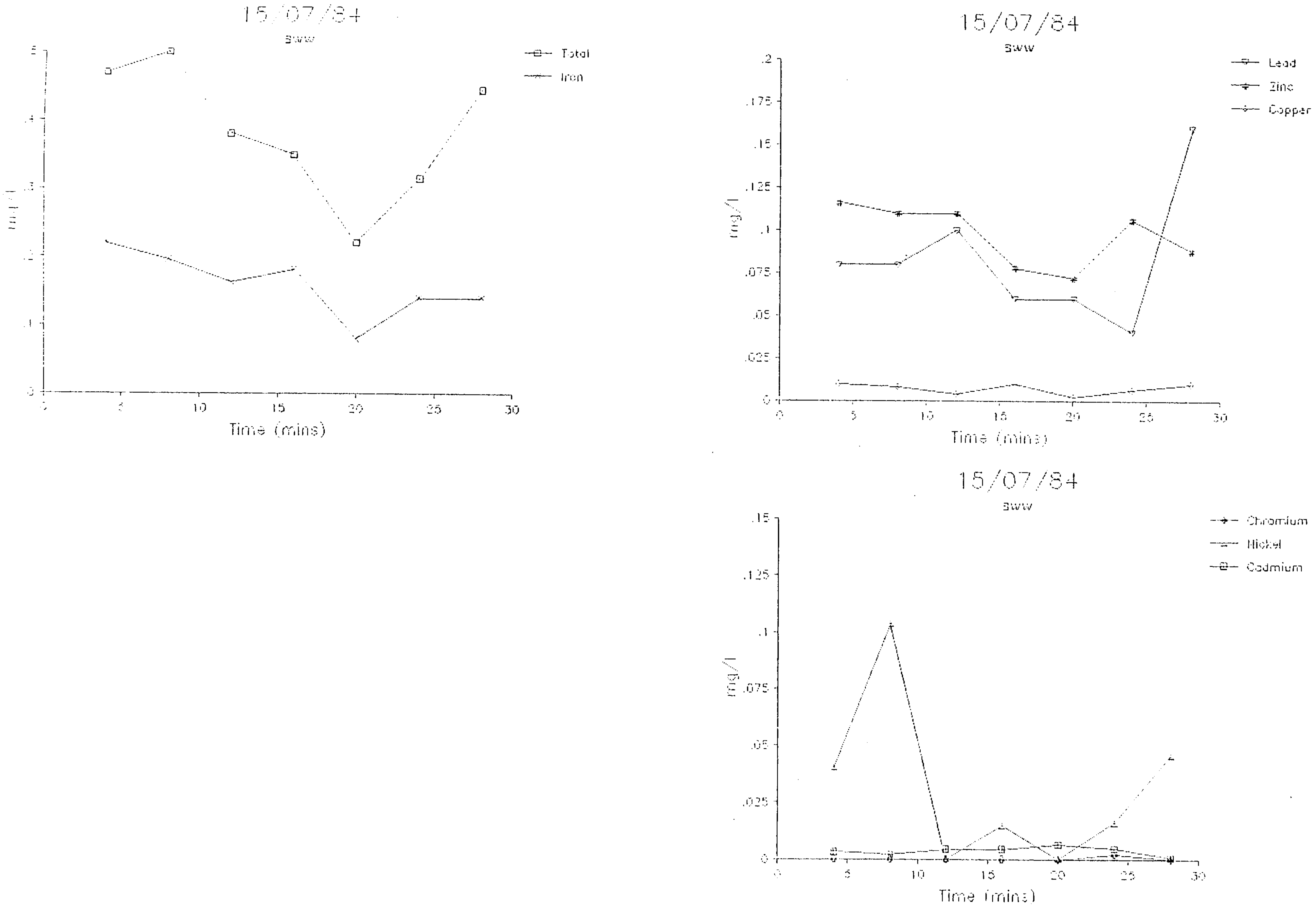


Figure 12.15 cont.

mg/l was observed 24 minutes into the storm period.

12.1.17 Discussion

Heavy metal concentrations were found to vary significantly both throughout individual runoff events and between storms. The relationship between water quality and the rate of flow was unique for each storm. In some instances the metal concentrations during the rising limb of the hydrograph were typically higher than those during the decending limb, suggesting a first flush effect (storms 3 and 6).

Within a given event, the peak metal concentrations did not always occur simultaneously for all metals. This may have been attributable to the differing origins of the various metals and their ease of mobilization within the catchment. Fletcher et al (1978) identified three principal types of pollutant runoff curve associated with source and removal coefficients of pollutants, which are illustrated in Figure 12.16. Curves one and two, in Figure 12.16, represent the behaviour of pollutants whose prime origin is the road surface or atmosphere. The ease of mobilization (removal coefficient) will determine which curve a pollutant will follow. A pollutant whose principal origin is from gully pot liquors will follow a type three curve.

Heavy metals might be expected to be concentrated in the first part of the storm event (Mance (1981)) as a result of the first flush effect. The first flush is accompanied by an initial high concentration of suspended solids, for which the metals have a strong affinity (Bourcier and Sharma (1980) and Wilber and Hunter (1979)), which often parallels the storm hydrograph.

Figure 12.16 Pollutant runoff curves - runoff event 6/1/76 Clifton Grove, Nottingham (Fletcher et al (1978))

Although the presence of a first flush was found in a few of the storms studied it was not the norm for all those analysed. This apparent discrepency would suggest that metal inputs were being delivered from a variety of sources and were mobilized at different times during the storm event. As a result the metal inputs contributed to the storm hydrograph at different times.

In storm 11 the metal peak concentration coincided with the peak flowrate, whilst in other storms the metal concentration peaked before the maximum flowrate (e.g. storms 2 and 12) and in some cases the peak concentration was observed after the peak flowrate (e.g. storm 4).

The soluble metal concentrations were often found to follow a similar pattern to that exhibited by the particulate concentrations, as was the case in storms 5 and 6. Soluble metal concentrations of zinc and copper were often closely related, suggesting a common source for the two metals.

Cadmium concentrations, and to a lesser extent chromium concentrations were found to peak much later during the storm event. Ellis (1982) suggested that this was probably due to the fact that these pollutants were associated with different contributing areas within the catchment and were thus loaded onto the hydrograph when that particular contributing area became effective. This could have been the case in the study due to the large extent of the catchment.

During a small number of the storm events studied no distinct patterns were displayed by the metal concentrations (for example storm 7), and the variations in metal concentrations within each of these storm events appeared to be totally random. This could have been due to a large number of interacting variables such as localized sources of pollutants, which would have tended to mask the identification of any evidence to suggest a pattern of behaviour.

Turbidity and conductivity was often found to display an inverse relationship with one another, an example where this was observed was storm 12.

In conclusion each storm event was unique in nature and it would therefore be impossible to draw any generalized conclusions for all of the storm events studied. The concentrations of pollutants were dependent upon a wide variety of factors including the time since the previous rainfall event, the duration and intensity of the previous and current rainfall event, and the retention times in branches of the sewer system (Mance (1981)).

A number of storms displayed secondary and multiple peaks in metal concentration. Storms 1 and 2 showed distinct secondary metal concentration peaks which were independent of any change in the flowrate, they were however, of smaller magnitude than the initial peaks.

The snowmelt runoff hydrograph for event 10 also displayed additional peaks which were independent of any increase in the flowrate, as was the case for storms 7 and 14. This was probably due to sporadic inputs from within the catchment which were loaded onto the runoff hydrograph at different times within the event.

The analysis of the pollutographs obtained from event 6 suggested that there were three possible mechanisms at work which could explain the temporal variation of pollutant loadings during a stormwater runoff event. Firstly, metal loadings peaked at the very start of the event, as any deposits within the sewer were washed out or from roof runoff, corresponding to the first flush. The initial peak was followed by the main peaks in metal concentrations, apparently unrelated to the flowrate but since this corresponded to the time of concentration of the catchment, approximately 90 minutes, it probably occurred when the whole catchment was contributing. Finally, a third peak occurred which corresponded more closely with the flowrate, suggesting that the heavier or more stubborn pollutants had been mobilized by the more intense rainfall and increased runoff velocities.

12.2 Soluble:Particulate Metal Ratios

The ratios of the cumulative soluble to the cumulative particulate total metal concentrations were plotted against time for each individual storm. Total metal concentrations were used to give an overall indication of the changes that occurred. Each storm portrayed different ratios, all of which varied throughout the duration of the storm.

Storm 1 displayed the highest soluble:particulate ratio at the start of the storm (approximately 3:1), however, after 12 minutes the value decreased to a level of approximately 2.15:1, where it remained for the duration of the storm (see Figure 12.17).

A similar pattern was observed for storm 2 but the ratios were much lower i.e. 0.25:1, indicating that there were greater concentrations of solids during the storm. The highest ratio, 0.36:1 was observed at the start of the storm and after 12 minutes the ratio decreased to a value of 0.22:1.

At the start of storm 3 the soluble to particulate ratio decreased from a value of 0.95:1 to 0.8:1 after a period of 10 minutes. The ratio then steadily increased to a maximum value of 1.5:1 after a time of 72 minutes. For the remainder of the storm the value of the ratio fluctuated about 1.3:1. An overall average value for the entire storm was approximately 1.2:1.

Storm 4 experienced very low soluble:particulate metal concentration ratios throughout the entire event. The highest values were observed at the begining of the storm and the overall average was found to be 0.325:1 (i.e. approximately 3:1 particulate:soluble ratio).

Peak soluble:particulate metal concentration ratios were observed after a time of 10 minutes during storm 5 with a value of 2.5:1. The value then dropped to 1.25:1 after a period of 23 minutes, which mirrored the time of the first flush as determined in Section 12.7. From 23 minutes onwards the ratio remained sensibly constant at a value of 1.2:1. The mean value for the entire storm was 1.5:1.

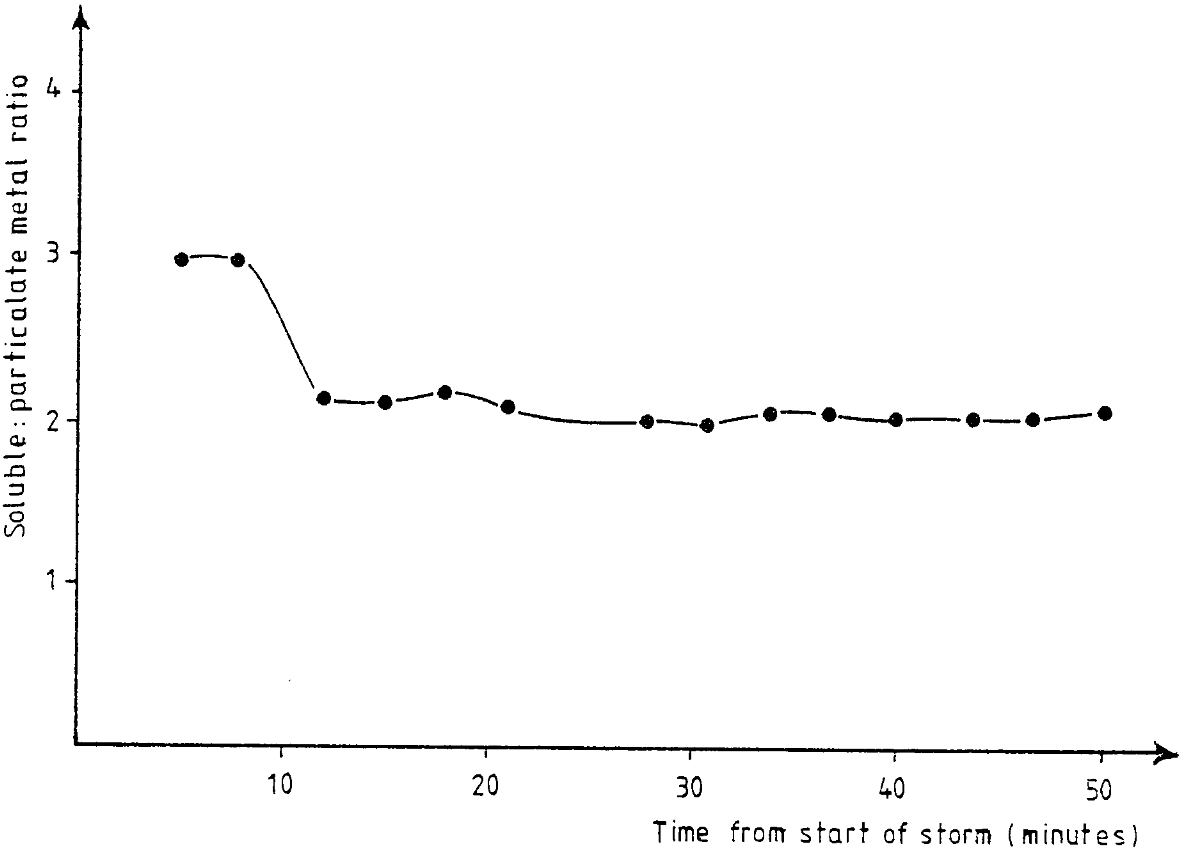


Figure 12.17 Soluble:particulate metal ratios for Storm 1 (16/8/83).

Storm 6 displayed an undulating pattern for the soluble:particulte metal ratios and the average for the entire storm event was 1.5:1 as was the case for storm 5.

The soluble:particulate metal ratios for storm 7 gradually increased from 1.25:1 to 1.6:1 throughout the storm, with an overall mean value of 1.4:1. Storm 8 displayed a similar pattern to that of storm 7 but the ratio decreased slightly after a time of 7 minutes. The average value for storm 8 was 2:1.

As was the case with storm 6, storm 9 showed an undulating pattern of behaviour. High soluble:particulate metal ratios were observed in this storm which had a mean value of approximately 3:1.

Very low soluble:particulate metal ratios which displayed little variation were observed for the entire duration of event 10. The mean ratio was approximately 0.435:1. A similar pattern was also noted for storm 11 which had a mean value of approximately 0.5:1.

A similar trend to that observed for storm 5 was also displayed by storm 12. A peak ratio of 1.3:1 was observed after a period of 9 minutes, which was followed by a decrease to a minimum value of 0.8:1 at a time of 49 minutes, thereafter the ratio continued to gradually increase. The mean for the storm event was approximately 0.9:1.

The soluble:particulate metal concentrations for storm 13 gradually increased throughout the storm with an overall mean ratio of 1:1. For the duration of storm 14, which occurred on the same day as storm 13, the ratios tended to increase slightly but were much lower with an average value of 0.5:1, i.e. 2:1 for the particulate:soluble ratio.

Storm 15 displayed the lowest soluble:particulate metal ratio for the entire sampling period. The ratio remained fairly constant throughout the storm and averaged approximately 0.13:1, i.e. approximately 7.5:1 particulate:soluble metals.

Five general patterns of behaviour were observed which described the variation of the soluble:particulate metal concentration ratios with time elapsed throughout a runoff event. These will now be described.

A slight increase in the ratio at the start of the storm followed by a rapid decrease was observed for storms 1, 5 and 12. This suggested that the soluble metals were discharged very rapidly initially, after which the particulate metals were discharged forcing the soluble:particulate ratio down. The opposite was seen to occur for storm 3, where there was a slight decrease in ratio at the start of the storm followed by an increase, suggesting that the soluble metals were discharged at a slightly later time. This may have been due to the ease of solubilization, since a period of time is required to allow the metals to escape into solution before being discharged.

An overall decrease in the soluble:particulate metal concentration was observed in a number of storms, namely storms 2, 4, 7, 8 and 13. This indicated that the soluble metal concentration were gradually reduced during the duration of the storm whilst the particulate metals increased. This may have been due to the times of mobilization within the catchment, since the soluble metals would probably be more readily removed and pass through the system whereas the particulate metals would require more time to become mobilized and transported through the system.

Storms 6 and 9 displayed rather undulating patterns of behaviour for the soluble:particulate metal concentration ratios, whereas storms 10, 11, 14 and 15 exhibited fairly uniform ratios throughout.

The actual soluble:particulate ratio tended to vary from one storm to another. For storms 1, 5, 6, 7, 8, 9 and 13 the average ratios were greater than one and for storms 2, 4, 10, 11, 14 and 15 the values were less than one, whilst for storms 3 and 12 the mean ratio was approximately 1:1.

The soluble:particulate metal concentration ratios not only varied from one storm event to another but also within given storm events. This could have been due to a number of factors including rainfall intensity, runoff velocity, wetness of the catchment (affecting solubility), the length of the antecedent dry period (affecting the build up of pollutants) and the catchment characteristics (affecting the time of travel of the pollutants).

It should be stressed, however, that care should be taken when comparing the particulate and soluble concentrations since both were measured in mg/l. The actual concentrations of metals within the particulates themselves (mg/kg) will obviously differ from those quoted herein. Furthermore, only the total metal concentrations were analysed for and the soluble:particulate metal concentration ratios for individual metals would have differed substantially from those quoted, since total metals reflect iron and therefore do not indicate variations in other metals. Individual metals were not studied due to the time constraints of the project, but it is hoped that this will form a topic for further research.

12.3 Metal Proportions

Metal proportions were calculated for each of the heavy metals analysed for in all the stormwater samples. The proportions were expressed as percentages.

The proportions for each metal tended to display considerable variation throughout the duration of an event and also between individual storm events. A summary Table, illustrating the maximum, minimum and mean metal concentrations for all the storm events is also given in Table 12.1. It can be seen from the Table that the range of variation of metal proportions were at times of great magnitude, for example soluble nickel ranged from zero to 58%.

From consideration of Table 12.1 it can be seen that the total iron concentration displayed the highest percentage values with a mean percentage of 76%, this was followed, in decreasing order of magnitude, by lead, zinc, nickel, copper, chromium and cadmium. The soluble metal concentrations followed a similar trend, whilst for the particulate metals the mean iron percentage was 95%, which was then followed in decreasing order of magnitude by lead, zinc, chromium, copper, nickel and cadmium.

METAL		PERCETAGES			
		MAX.	MIN.	MEAN	STD.DEV
Iron	P	99.17	64.22	95.11	2.90
	S	82.32	46.84	58.46	6.92
	T	95.24	45.24	76.34	8.22
Lead	P	11.61	-	1.41	0.83
	S	36.61	2.62	16.41	5.49
	T	23.13	1.20	7.81	2.92
Zinc	P	5.48	-	1.20	0.66
	S	46.77	-	12.01	7.63
	T	32.47	-	5.12	2.99
Copper	P	2.99	-	0.51	0.29
	S	15.96	0.41	3.07	1.12
	T	5.07	0.12	1.62	0.69
Chromium	P	5.84	-	0.61	0.41
	S	5.75	-	0.92	0.66
	T	5.27	-	0.82	0.46
Nickel	P	21.40	-	0.35	0.44
	S	58.11	-	7.41	5.85
	T	41.00	-	3.77	3.65
Cadmium	P	1.98	-	0.10	0.16
	S	4.84	-	0.34	0.35
	T	2.92	-	0.32	0.47

Table 12.1 Range of storm percentage data including iron.

Key: P = Particulate metal
S = Soluble metal
T = Total metal

STD.DEV = Standard Deviation

Variations were observed between the particulate and soluble metal concentration phases. The mean particulate iron percentage was found to be much greater than the soluble iron percentage with corresponding values of 95% compared with 58%. However, for all other heavy metal concentrations larger mean percentages were found to occur within the soluble phase. This may have been due to the fact that iron was so dominant in the particulate phase.

Since iron concentration was seen to predominate as previously described, the metal proportions were recalculated excluding the iron concentrations. A summary of the resulting values are presented in Table 12.2.

Lead and zinc proportions were now observed to predominate with mean total percentages of 11 and 14% respectively. Also the particulate proportions for both lead and zinc were seen to be of the same order of magnitude with percentage values of 31 and 30% respectively. The lead and zinc proportions were followed in decreasing order of magnitude by chromium, copper, nickel and cadmium. The highest percentage observed within the soluble phase was that of lead with a mean percentage of 41%, this was then followed by zinc, nickel, copper, chromium and finally cadmium.

With the exclusion of iron from the data set, higher mean metal proportions were observed for zinc, copper, chromium and cadmium in the particulate phase and higher mean proportions were observed for lead and nickel in the soluble phase. The average zinc percentages were, however, of similar magnitude in both the particulate and soluble phases, with values of 30 and 29% respectively.

METAL		PERCETAGES			
		MAX.	MIN.	MEAN	STD.DEV
Lead	P	81.08	-	31.36	12.53
	S	73.51	3.53	41.25	11.11
	T	73.37	5.90	41.05	10.96
Zinc	P	75.31	-	30.11	13.49
	S	80.05	-	29.34	15.31
	T	78.66	-	28.71	14.44
Copper	P	50.00	-	12.87	4.76
	S	30.28	1.42	7.80	2.31
	T	23.94	0.58	8.30	1.83
Chromium	P	61.73	-	15.05	6.13
	S	12.47	-	2.432	1.62
	T	38.03	0.24	4.04	1.47
Nickel	P	59.30	-	7.13	6.50
	S	84.76	-	18.31	13.67
	T	83.66	-	16.70	12.63
Cadmium	P	35.09	-	2.77	4.14
	S	1.46	-	0.83	0.76
	T	12.01	-	1.14	1.00

Table 12.2 Range of storm percentage data excluding iron.

Key: P = Particulate metal
S = Soluble metal
T = Total metal

STD.DEV = Standard Deviation

12.3.1 Discussion

Since the range of variation of metal proportions within specific storm events and between events was so large, little could be concluded from the results.

Iron was the major contributor of the heavy metals in the stormwater runoff samples analysed. When iron was eliminated from the calculations, lead and zinc were found to account for approximately 70% of the total metals discharged. Cadmium was found to account for only a small percentage, approximately 1%.

12.4 Correlations between Metal Concentrations

Although heavy metal concentrations were found to display considerable variation throughout individual storm events and between events, some time related trends were found to exist within individual storm events.

Correlation matrices were computed for each individual storm event, for each of the total, particulate and soluble metal concentrations. Recorded data for the Phox parameters were available for eleven storms out of the total of fifteen storms analysed. The Phox parameters, where included, were correlated against the total metal concentrations. Listed below are the parameters included in the calculations used to determine the correlation matrices:

a) time from the start of the storm (TSTART),

b) flowrate (FLOW),

c) iron, lead, zinc, copper, chromium, nickel and cadmium,

d) DO, pH, temperature, chloride, conductivity and turbidity.

The correlations between the various parameters varied considerably between individual storms and between the metal phases. Some storms had virtually all parameters well correlated for example storm 2 (16/09/83) displayed significant correlations between all the particulate metals, see Table 12.3. Other storms displayed only a few well correlated parameters for example storm 3 (10/10/83). This would appear to indicate that a number of factors influenced the metal concentrations during individual storm events.

A number of good correlations (i.e. correlation coefficients varying between 0.80 and 0.99) were seen to consistently occur for several storms, these are illustrated in Table 12.4. The most commonly occurring correlation was found to be between total iron and the total metal concentrations, and was observed in 93% of the storms analysed. This would be expected since iron was the most predominant metal in all the storm events (Section 12.3) and therefore formed a major part of the total metal concentration. The concentration of iron was also seen to be fairly consistently correlated to those of lead, zinc and copper, possibly indicating a common source of the metals within the stormwater runoff.

Most metals in fact appeared to be well correlated with the overall total metal concentrations for each of the individual storms analysed. Particulate lead concentrations were well correlated with those of zinc, copper, chromium and total metals in approximately 50% of the storms. Particulate zinc to copper concentrations were seen to be well correlated in 70% of the storms and particulate zinc to total particulate concentration were well correlated in 80% of the cases. Soluble chromium to nickel concentrations were seen to be significantly correlated in 40% of the storms.

	TSART	FLOW	FE	PB	ZN	CU	CR	NI	CD	TOT
TSART	1.0									
FLOW	- 0.49	1.0								
FE	- 0.89	0.71	1.0							
PB	- 0.91	0.64	0.97	1.0						
ZN	- 0.91	0.65	0.99	0.99	1.0					
CU	- 0.88	0.68	0.98	0.99	0.99	1.0				
CR	- 0.74	0.65	0.91	0.84	0.88	0.84	1.0			
NI	- 0.86	0.63	0.89	0.91	0.91	0.92	0.74	1.0		
CD	- 0.42	0.42	0.40	0.35	0.42	0.44	0.36	0.32	1.0	
TOT	- 0.89	0.71	0.99	0.97	0.99	0.98	0.91	0.89	0.40	1.0

Table 12.3 Correlation matrix between various parameters and particulate metals for storm 2 (09/16/83).

Key: TSTART = Time from start of storm
TOT = Total metal concentration

CORRELATION BETWEEN	OCCURRENCE IN STORMS (%)		
	TOTAL	PARTICULATE	SOLUBLE
TSTART:FLOW	60	-	-
:TEMP	64	-	-
:TURB	54	-	-
FLOW:TEMP	45	-	-
DO:TEMP	36	-	-
PH:TEMP	36	-	-
FE:PB	40	47	47
:ZN	73	80	47
:CU	40	60	13
:TOT	93	67	80
PB:ZN	40	33	47
:CU	33	53	20
:CR	13	40	13
:TOT	47	47	53
ZN:CU	53	67	40
:TOT	67	80	67
CU:TOT	40	60	20
CR:NI	33	7	40
:TOT	20	40	27

Table 12.4 Percentile number of storms where correlation coefficients of 0.80 and 0.99 were observed between various paramters and total, particulate and soluble metal concentrations.

Key: TSTART = Time from start of storm
TEMP = Temperature
TURB = Turbidity
DO = Dissolved oxygen
TOT = Total metal concentration

In most storms the various parameters were found to be well correlated with time, with correlation coefficients of between 0.6 and 0.8. Higher correlation coefficients (values between 0.80 and 0.99) were observed between, the time from start of the storm and flow (for 60% of the storms), time from start of the storm and temperature (a negative correlation for 64% of the storms), and time from start of the storm and turbidity (a negative correlation for 54% of the storms). The only other Phox paramters that were seen to give reasonable correlations in a number of storms (36%) were between dissolved oxygen and temperature, and pH and temperature. No relationship was found between the Phox parameters and the metal concentrations.

It should, however, be stressed at this point that during individual storm events some parameters were highly correlated to one another but were not common for the majority of storms and have therefore not been included in this discussion.

12.4.1 Seasonal Variations

In order to determine whether any seasonal variation was displayed between the correlation matrices, especially during the winter salting period, the percentage of storms where good correlations occurred were considered for the winter and summer periods.

The winter period was taken from October to March, the salting period being from November until March, and the summer period from April until September. Unfortunately no storms were analysed during the period when de-icing activity was at its peak (from mid February to the end of March) and it was therefore difficult to arrive at any meaningful conclusion.

Little marked differences were observed between the winter and summer periods. However, some of the correlations which occurred during the summer were not found during the winter months specifically those between: soluble lead and copper concentrations; total metal and soluble lead concentrations; total metal and chromium concentrations; soluble copper and total metal concentrations; particulate chromium and nickel concentrations; total chromium and total metal concentrations. These relationships could well have been due to the longer dry periods which occurred at this time, thus allowing larger deposits to accumulate than would be possible during the wetter winter months.

It was also noted that the frequency of good correlations between particulate metals was greater during the summer months the winter months. The soluble metals displayed little seasonal difference but gave slightly higher levels during the summer.

12.4.2 Discussion

The correlation matrices tended to vary from one storm to another and between the various metal phases within individual storms. However, in many cases the resulting correlation matrices showed that the metal concentrations correlated well with each other. A negative correlation between the metal concentration and the time from start of the storm was observed in a number of storms. Further, a large percentage of storms displayed a negative correlation, between the time from the start of the storm and the flowrate, and between the time from start of the storm and the temperature and turbidity.

Little seasonal variation within the correlation matrices was observed, however, this could have been due to the timing of the events sampled and the limited number of samples.

12.5 Average Stormwater Metal Concentrations

The quality of stormwater runoff has been shown to display considerable variation during the course of an event (Section 12.1), that differences between events, even at different times of the year, were often masked. As a result the average quality of each event was described by the flow weighted mean concentration.

12.5.1 Flow Weighted Mean Concentration

The flow weighted mean concentration was determined by multiplying each metal concentration by the discharge rate with which it was associated, summing all products and dividing by the summation of discharge rates (Bryan (1972)). The results are presented in Table 12.5 and in Figure 12.18.

From consideration of the Table it can be seen that the flow weighted mean concentrations varied greatly from one storm event to another. However, some events which possessed different characteristics actually discharged effluents of a similar quality, for example storms 11 and 14.

A summary of Table 12.5 is given in Table 12.6, which presents the average flow weighted mean metal concentrations for the catchment. It has been suggested by Mance (1981) that for a particular catchment there is a reasonably consistent flow weighted mean concentration for each pollutant. However, the values observed in this study were shown to display quite a considerable variation.

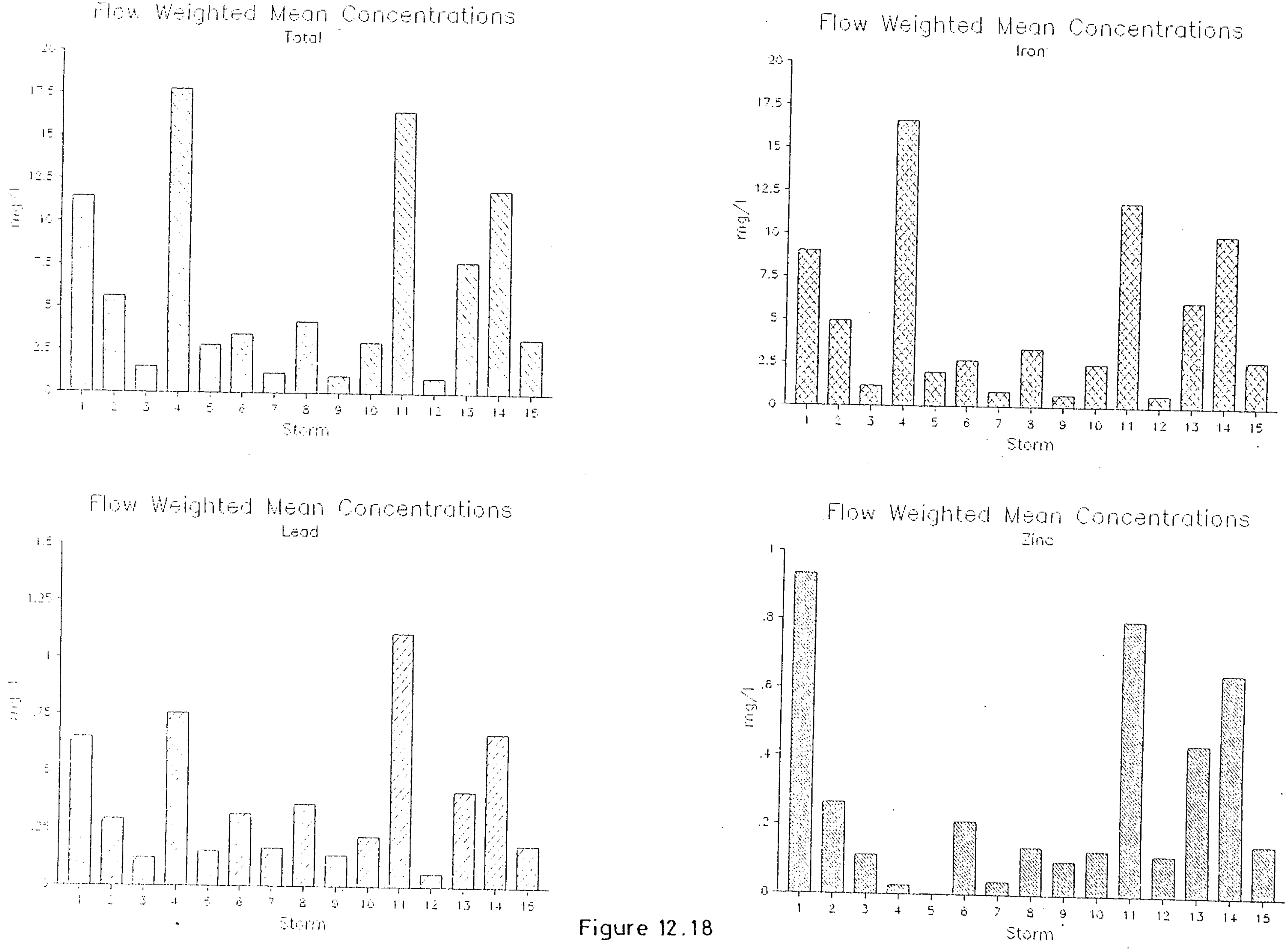
STORM		IRON	LEAD	ZINC	COPPER	CHROMIUM	NICKEL	CADMIUM	TOTAL
1	P	3.51	0.052	0.054	0.030	0.020	0.003	0.0002	3.67
	S	5.49	0.598	0.879	0.173	0.077	0.055	1.0625	7.77
	T	8.99	0.650	0.933	0.203	0.097	0.058	1.0630	11.44
2	P	4.26	0.066	0.080	0.017	0.015	0.010	0.0007	4.45
	S	0.65	0.224	0.184	0.051	0.006	0.056	0.0028	1.18
	T	4.91	0.290	0.264	0.069	0.021	0.066	0.0035	5.62
3	P	0.61	0.007	0.005	0.002	0.004	0.008	0.0013	0.67
	S	0.53	0.114	0.108	0.032	0.007	0.031	0.0014	0.83
	T	1.14	0.121	0.113	0.034	0.010	0.040	0.0027	1.50
4	P	13.16	0.253	0.008	0.094	0.038	0.024	0.0015	13.58
	S	3.01	0.501	0.018	0.072	0.053	0.478	0.0035	4.14
	T	16.17	0.754	0.026	0.166	0.091	0.502	0.0050	17.72
5	P	1.20	0.009	0.001	0.003	0.013	0.010	0.0003	1.24
	S	0.77	0.142	0.003	0.053	0.051	0.533	0.0009	1.54
	T	1.97	0.152	0.003	0.056	0.064	0.543	0.0012	2.78
6	P	1.41	0.032	0.021	0.016	0.011	0.001	0.0002	1.49
	S	1.24	0.281	0.192	0.044	0.023	0.167	0.0011	1.95
	T	2.63	0.313	0.213	0.060	0.034	0.169	0.0013	3.44
7	P	0.43	0.001	0.003	0.001	0.002	0.000	0.0015	0.44
	S	0.42	0.164	0.034	0.028	0.005	0.030	0.0058	0.69
	T	0.86	0.165	0.037	0.029	0.007	0.030	0.0073	1.13
8	P	2.72	0.034	0.032	0.008	0.012	0.001	0.0002	3.00
	S	0.65	0.320	0.107	0.032	0.008	0.077	0.0026	1.20
	T	3.37	0.354	0.139	0.039	0.020	0.078	0.0028	4.20
9	P	0.23	0.004	0.005	0.002	0.004	0.003	0.0018	0.25
	S	0.43	0.130	0.093	0.022	0.003	0.016	0.0047	0.70
	T	0.66	0.134	0.098	0.024	0.007	0.019	0.0065	0.95
10	P	1.94	0.020	0.026	0.005	0.007	0.004	0.0005	2.00
	S	0.56	0.200	0.104	0.024	0.009	0.047	0.0021	0.95
	T	2.51	0.220	0.130	0.029	0.017	0.051	0.0026	2.95
11	P	8.90	0.305	0.181	0.099	0.042	0.029	0.0025	11.85
	S	3.04	0.803	0.618	0.073	0.010	0.083	0.0085	4.64
	T	11.94	1.108	0.799	0.173	0.052	0.113	0.0110	16.49
12	P	0.45	0.006	0.005	0.002	0.001	0.002	0.0015	0.46
	S	0.20	0.057	0.115	0.025	0.003	0.013	0.0017	0.42
	T	0.63	0.057	0.120	0.027	0.004	0.014	0.0032	0.88

Table continued overleaf

STORM		IRON	lEAD	ZINC	COPPER	CHROMIUM	NICKEL	CADMIUM	TOTAL
13	P	3.65	0.044	0.051	0.032	0.028	0.006	0.0017	3.81
	S	2.50	0.371	0.390	0.090	0.060	0.470	0.0031	3.88
	T	6.14	0.415	0.441	0.122	0.088	0.476	0.0048	7.69
14	P	7.57	0.110	0.105	0.037	0.044	0.021	0.0005	7.89
	S	2.50	0.555	0.543	0.094	0.033	0.258	0.0047	3.95
	T	10.04	0.665	0.648	0.131	0.077	0.279	0.0052	11.84
15	P	2.57	0.103	0.056	0.019	0.011	0.007	0.0006	2.77
	S	0.16	0.079	0.098	0.007	0.000	0.033	0.0038	0.38
	T	2.74	0.182	0.154	0.026	0.011	0.040	0.0044	3.15

Table 12.5 Flow weighted mean metal concentrations (mg/l).

Key: P = Particulate metal
S = Soluble metal
T = Total metal



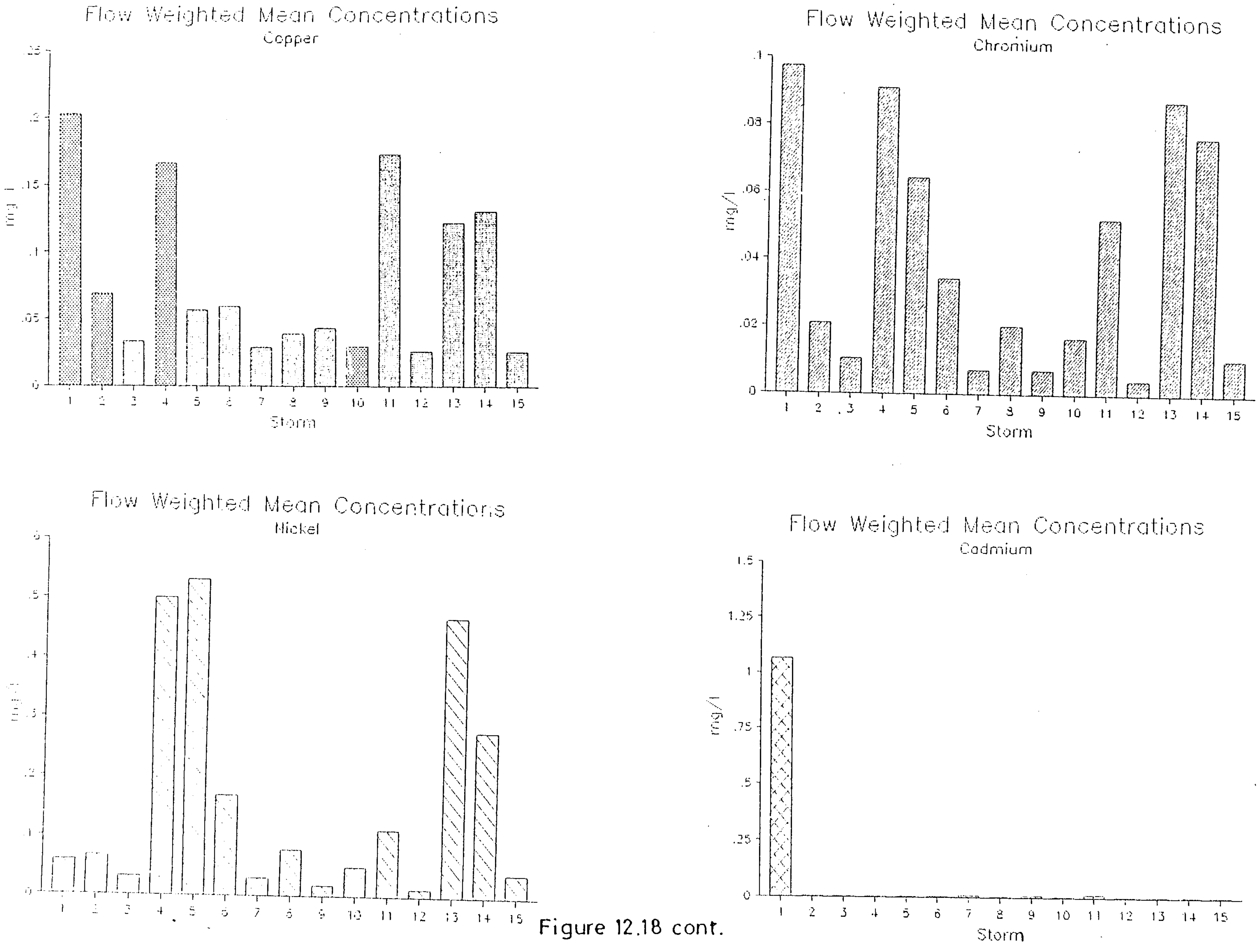


Figure 12.18 cont.

METAL		MAX.	MIN.	MEAN	STD.DEV.
Iron	P	13.16	0.229	3.510	3.690
	S	5.49	0.165	1.476	1.513
	T	16.17	0.657	5.015	4.814
Lead	P	0.30	0.000	0.069	0.092
	S	0.80	0.057	0.302	0.221
	T	1.11	0.057	0.372	4.863
Zinc	P	0.18	0.000	0.042	0.049
	S	0.88	0.003	0.232	0.257
	T	0.93	0.003	0.274	0.294
Copper	P	0.10	0.001	0.024	0.032
	S	0.17	0.007	0.055	0.042
	T	0.20	0.026	0.080	0.061
Chromium	P	0.04	0.001	0.017	0.014
	S	0.08	0.000	0.025	0.024
	T	0.10	0.004	0.040	0.034
Nickel	P	0.03	0.000	0.008	0.009
	S	0.53	0.013	0.156	0.186
	T	0.53	0.014	0.164	0.188
Cadmium	P	0.002	0.0002	0.001	0.0007
	S	1.062	0.0009	0.074	0.273
	T	1.063	0.0013	0.075	0.273
Total	P	13.58	0.250	3.840	4.13
	S	7.77	0.390	2.961	3.69
	T	17.72	0.882	6.120	5.65

Table 12.6 Summary of flow weighted mean metal concentrations (mg/l).

Key: P = Particulate metal
S = Soluble metal
T = Total metal

The average stormwater metal concentrations were also determined by integration of the area beneath each storm loading curve and subsequent division of the total loads produced by the total flows measured (Helsel et al (1974)). The results for the total metals are presented in Table 12.7. From consideration of Tables 12.5 and 12.7, it can be seen that for the majority of storms the values were of a similar order of magnitude therefore validating data set.

12.5.2 Comparison with other Studies

In order to compare the results obtained during the study of the Chelmsley Wood catchment with other related studies, summary Tables have been compiled which present the overall ranges of metal concentrations which have been observed in stormwater runoff. The data are presented in Tables 12.8 and 12.9 respectively.

It is difficult to make any direct comparisons with other studies since many authors do not state the form in which the metals exist, be it total, particulate or soluble. In addition each catchment is site specific and will only display metal concentrations characteristic of that particular area. Unless due consideration is taken, any comparison of metal concentrations between one catchment and another could be meaningless. Bearing this in mind however, from a study of Tables 12.8 and 12.9 a number of points are evident.

The ranges of metal concentrations cited in the literature were considerable, for example, the total iron concentration ranged from 1.0 to 85 mg/l. The maximum concentrations for total and soluble iron, lead, zinc, copper and chromium observed within this study fell within the bounds of the values quoted from in the literature. However, maximum levels recorded for total nickel and total cadmium

STORM	IRON	LEAD	ZINC	COPPER	CHROMIUM	NICKEL	CADMIUM	TOTAL
1	9.13	0.651	0.940	0.203	0.095	0.498	0.011	11.53
2	4.96	0.295	0.268	0.069	0.021	0.073	0.003	5.69
3	1.50	0.128	0.102	0.030	0.009	0.029	0.002	1.80
4	15.72	0.749	0.027	0.142	0.077	0.432	0.005	17.16
5	2.06	0.159	0.003	0.059	0.059	0.478	0.002	2.82
6	2.72	0.309	0.211	0.333	0.159	0.159	0.001	3.99
7	0.88	0.166	0.039	0.030	0.006	0.031	0.017	1.16
8	3.44	0.360	0.142	0.039	0.020	0.081	0.002	4.09
9	0.66	0.137	0.097	0.024	0.007	0.018	0.006	0.95
10	2.53	0.219	0.131	0.028	0.017	0.052	0.002	2.98
11	10.49	0.957	0.713	0.152	0.046	0.102	0.009	12.47
12	0.64	0.058	0.114	0.026	0.008	0.013	0.002	0.86
13	6.69	0.440	0.454	0.134	0.091	0.486	0.006	8.30
14	10.24	0.653	0.667	0.134	0.073	0.280	0.005	12.05
15	25.51	0.174	0.151	0.024	0.011	0.058	0.004	25.94

Table 12.7 Average total metal concentrations (mg/l).

METAL		MAX.	MIN.	MEAN (flow weighted)
Iron	P	29.45	0.118	3.510
	S	9.20	0.080	1.476
	T	33.47	0.310	5.015
Lead	P	0.67	0.000	0.069
	S	1.32	0.002	0.302
	T	2.18	0.024	0.372
Zinc	P	0.29	0.000	0.042
	S	1.35	0.000	0.232
	T	1.43	0.000	0.274
Copper	P	0.21	0.000	0.024
	S	0.22	0.002	0.055
	T	0.32	0.002	0.080
Chromium	P	0.07	0.000	0.017
	S	0.02	0.000	0.025
	T	0.25	0.000	0.040
Nickel	P	0.05	0.000	0.008
	S	1.51	0.000	0.156
	T	1.52	0.000	0.164
Cadmium	P	0.009	0.000	0.001
	S	0.052	0.000	0.074
	T	1.545	0.000	0.075
Total	P	30.15	0.14	3.84
	S	13.35	0.22	2.96
	T	35.34	0.43	6.12

Table 12.8 Range of Stormwater Data (mg/l).

Key:
P = Particulate metal
S = Soluble metal
T = Total metal

METAL		STORMWATER RUNOFF			ROAD/MOTORWAY RUNOFF		
		Max.	Min.	Mean	Max.	Min.	Mean
Iron	T	85.00	1.00	0.32 - 38	440.00	0.67	0.64 - 76
	S	500.00	-	190 - 560	-	-	-
Lead	T	26.00	0.05	0.10 - 0.46	14.73	0.003	0.15 - 10
	S	1800.00	10.00	10 - 42	1200.00	3.00	-
Zinc	T	4.60	0.008	0.12 - 1.6	22.00	0.01	0.25 - 10
	S	1200.00	15.00	40 - 290	-	-	-
Copper	T	4.62	0.001	0.03 - 0.54	1.70	0.003	0.05 - 0.1
	S	20.00	4.00	0 - 4	-	-	-
Chromium	T	0.47	0.003	0.002 - 0.34	0.85	0.018	0.08 - 0.4
	S	-	-	10 - 80	-	-	-
Nickel	T	0.29	0.006	0.02 - 0.24	-	-	-
	S	-	-	6	-	-	1.55
Cadmium	T	0.008	0.0006	0.006 - 0.016	13.73	0	0.003 -0.01
	S	5.00	0.50	1 - 9.1	-	-	-

Table 12.9 Metal concentration ranges (mg/l) from the literature. (adapted from Tables 4.5 and 4.8)

Key: T = Total metal
S = Soluble metal

were higher than those found in the majority of related stormwater runoff studies. The values do, however, fall within the ranges quoted for road/motorway surface runoff. However, the maximum recorded total cadmium concentration for this study was 1.545 mg/l, and was much lower than the maximum value (13.73 mg/l) observed for road/motorway runoff.

The Tables show the metal concentrations obtained in this study are fairly typical of those found in other stormwater quality studies. However, by comparison with other studies levels of nickel and cadmium are abnormal for the type of catchment concerned. The maximum concentrations of nickel and cadmium were attained in November (storms 5 and 6) during the period of road salting. As a result the elevated concentrations of these two metals could have been due to the use of road salt. If the values for nickel and cadmium were excluded from the analysis, all the data would then fall within the ranges quoted in other sources of reference on stormwater runoff quality.

12.5.3 Discussion

The average concentrations of heavy metals in urban stormwater runoff do not provide an adequate description of the runoff hydrograph as wide variations in metal concentration exist during any individual event, a view supported by Waller (1972). However, they enable a comparison with data from other studies and catchments to be made.

12.6 Total Storm Loads

In order to assess the quantity of pollutants discharged during each storm event, it was necessary to relate sample quality and runoff volume.

Quality and quantity data were both available for each of the storm runoff events studied. In order to calculate the total load, the volume of runoff and pollutant concentrations over a time interval (t) were assumed to be the average of the levels recorded at t_0 and t_1. Therefore in any time interval the load could be expressed according to the equation:

$$\text{Load} = \frac{(q_0 + q_1)}{2} \times \frac{(C_0 + C_1)}{2} \times t \qquad (\text{mg}) \qquad (12.1)$$

where: q_0 is the discharge at t_0 (l/s),

q_1 is the discharge at t_1,

C_0 is the pollutant concentration at t_0 (mg/l),

C_1 is the pollutant concentration at t_1,

t is the time interval (seconds).

The total load for the storm duration is given by:

$$\text{Total Load} = \sum_{t_0}^{tn} \frac{(q_0 + q_1)}{2} \times \frac{(C_0 + C_1)}{2} \times t \qquad (12.2)$$

where: $t_n - t_0$ represents the storm duration.

The total metal loads for each storm studied were calculated through the application of equations (12.1) and (12.2). The calculations were performed on a microcomputer and the results are presented in Table 12.10.

STORM		IRON	LEAD	ZINC	COPPER	CHROMIUM	NICKEL	CADMIUM	TOTAL
1	P	1397	20.62	21.42	11.86	8.19	1.18	0.14	1460
	S	2159	233	345	67.19	28.68	193	3.99	3029
	T	3556	254	366	79.05	36.87	194	4.14	4489
2	P	2306	36.29	43.61	9.58	8.15	5.40	0.33	2409
	S	365	123	100	27.89	3.23	33.79	1.61	654
	T	2671	160	144	37.47	11.43	39.18	1.94	3063
3	P	1364	16.86	10.43	3.56	8.20	1.81	2.18	1407
	S	2325	298	241	70.73	14.55	70.42	3.24	3023
	T	2689	315	251	74.29	22.75	72.23	5.42	4430
4	P	6683	115	4.78	42.71	18.56	11.97	0.67	6877
	S	1527	276	9.42	31.57	22.01	214	2.18	2082
	T	8210	391	14.20	74.28	40.57	226	2.85	8958
5	P	620	5.21	0.26	1.65	6.55	4.77	0.33	639
	S	392	72.83	1.26	27.44	22.81	230	0.94	747
	T	1012	78.04	1.52	29.10	29.36	235	1.27	1386
6	P	2737	51.54	36.05	25.18	18.58	2.42	0.33	2870
	S	2069	475	325	544	253	270	1.96	3937
	T	4805	527	361	569	271	272	2.29	6807
7	P	41.44	0.06	0.30	0.12	0.26	-	0.16	42.34
	S	40.62	15.51	3.43	2.69	0.35	2.90	1.43	66.93
	T	82.06	15.56	3.73	2.81	0.61	2.90	1.59	109
8	P	1151	14.22	13.71	3.17	5.22	0.36	0.07	1188
	S	265	134	44.70	13.22	3.10	33.02	0.84	494
	T	1416	148	58.41	16.39	8.32	33.39	0.91	1682
9	P	367	6.16	9.23	4.35	6.59	4.42	2.69	400
	S	706	216	148	34.53	5.28	24.64	7.87	1143
	T	1074	222	157	38.89	11.87	28.84	10.56	1544
10	P	2050	21.40	27.13	4.22	7.51	3.87	0.55	2115
	S	593	208	109	25.40	10.46	50.36	2.16	999
	T	2643	229	136	29.62	17.97	54.22	2.71	3114
11	P	25196	773	517	255	117	82.45	6.94	26947
	S	8044	2260	1744	229	29.17	239	22.35	12567
	T	33240	3033	2260	484	146	32	29.29	39514
12	P	366	0.06	3.86	1.41	3.66	1.26	0.51	377
	S	157	47.20	88.77	19.83	2.60	8.97	1.40	326
	T	523	47.26	92.63	21.24	6.26	10.24	1.91	703

Table continued overleaf

STORM		IRON	LEAD	ZINC	COPPER	CHROMIUM	NICKEL	CADMIUM	TOTAL
13	P	477	5.42	5.07	4.23	3.57	0.79	0.27	497
	S	327	47.45	49.46	11.92	7.37	57.65	0.44	501
	T	804	52.86	54.52	16.15	10.94	58.44	0.70	998
14	P	3741	42.84	52.02	18.12	19.85	10.27	0.37	3885
	S	1222	274	272	47.07	15.35	126	2.26	1958
	T	4963	316	324	65.19	35.20	136	2.63	5843
15	P	5932	22.94	12.68	4.01	2.44	6.32	0.14	5980
	S	37.66	17.70	22.64	1.57	0.06	7.31	0.93	87.87
	T	5970	40.64	35.32	5.58	2.50	13.63	1.07	6068

Table 12.10 Calculated total storm loads for sampling period (g). (values are rounded values for ease of presentation)

Key: P = Particulate metal
S = Soluble metal
T = Total metal

12.6.1 Soluble:Particulate Metal Loadings

From consideration of Table 12.10 it can be seen that the majority of the metals, i.e. lead, zinc, copper, nickel and cadmium, were generally found in greater loadings within the soluble phase than in the particulate phase. However, iron displayed greater loadings within the particulate phase which may reflect its origin as being mainly from the soil and the fact that it is less soluble than some of the other metals.

Although the ratio of the soluble to particulate loads show variation, the ratios are generally within one or two orders of magnitude. In storms 8, 10, 11 and 14, the soluble:particulate ratio was approximately 1:2, whereas in storms 1 and 3 the ratio was 2:1. One obvious abnomality was that of storm 15, which had a ratio of 1:60. This was a unique storm of short duration but with fairly high rainfall intensities, which probably produced sufficient energy to mobilize surface contaminants and transport them quickly to the sewer system before solubilization occurred.

12.6.2 The Total Metal Storm Loads

The total heavy metal loadings for the individual storms are illustrated in Figure 12.19 and were presented in Table 12.10.

Heavy metal loadings during individual storm events were shown to display quite considerable variation. The highest single storm load was recorded for storm 11 on 24/05/84, which produced in total, nearly 40 kg of the heavy metals analysed for in this study. Of the total approximately 33 kg was iron, 3 kg lead, 2 kg zinc and 0.5 kg copper. This high storm load was due to an abnormally high rainfall intensity, which reached nearly 50 mm/hr and produced a maximum flowrate of over 2000 l/sec, quite uncommon for this catchment. The high rainfall intensity and flowrate would have produced sufficient energy for the efficient and rapid removal of contaminants from surfaces within the catchment and from within the sewer system (including the gully pots), and hence produced high metal loads.

The minimum storm loads generated occurred during the first storm on 17/12/83, which produced only 109 gms of total metals. The storm was characterized by low total rainfall and rainfall intensity and hence subsequent low flowrates and volumes.

The inherent variability in the heavy metal pollutant loads have also been found in other related studies, and were shown in Tables 4.10 and 4.13 and are probably a result of a number of factors (Wilber and Hunter (1975)):

a) the length of the antecedent dry period,
b) the intensity and duration of the storm event,
c) the size of the drainage basin,
e) land use,

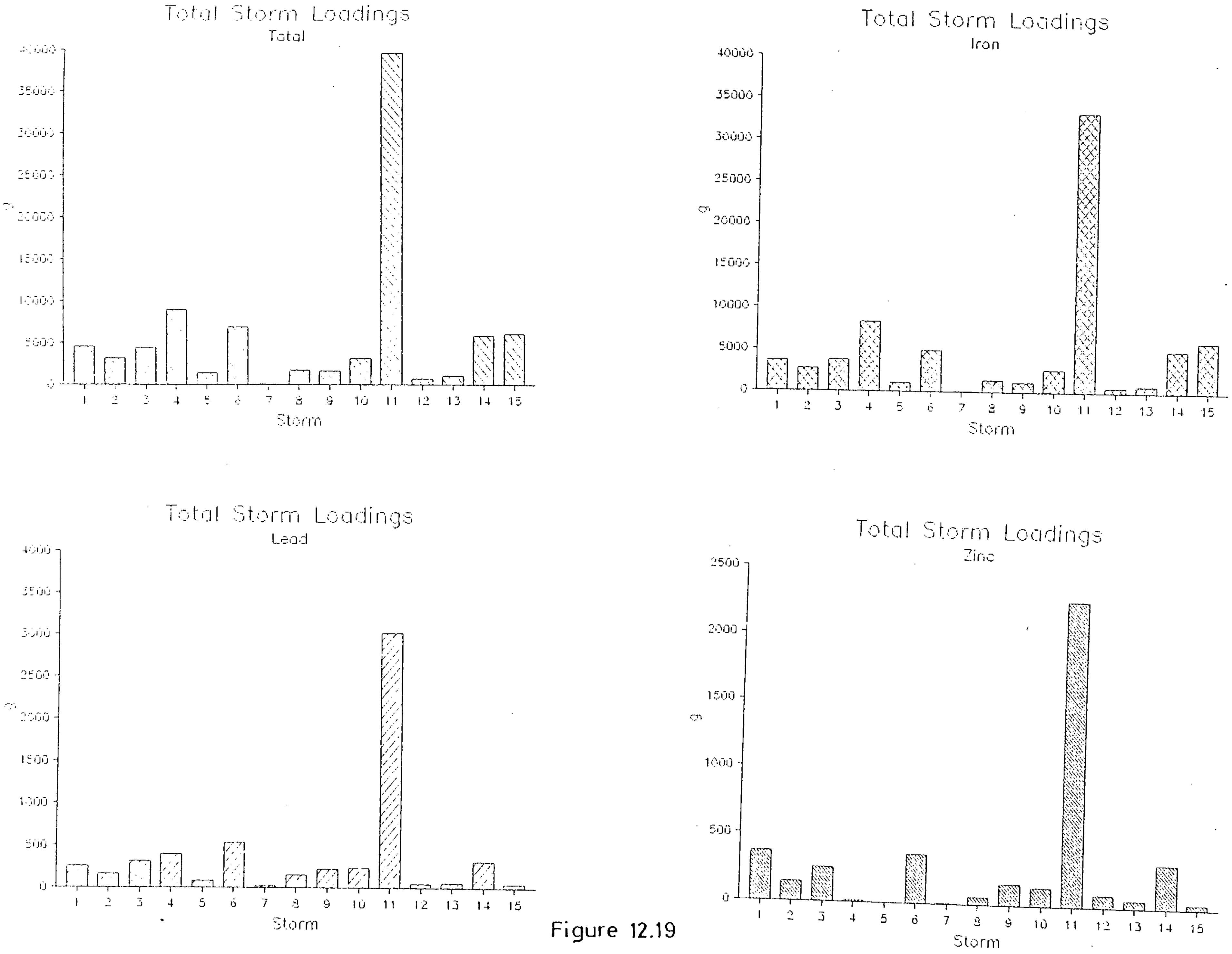

Total Storm Loadings
Total
g
0
5000
10000
15000
20000
25000
30000
35000
40000
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
Storm
Total Storm Loadings
Iron
g
0
5000
10000
15000
20000
25000
30000
35000
40000
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
Storm
Total Storm Loadings
Lead
g
0
500
1000
1500
2000
2500
3000
3500
4000
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
Storm
Total Storm Loadings
Zinc
g
0
500
1000
1500
2000
2500
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
Storm

Figure 12.19

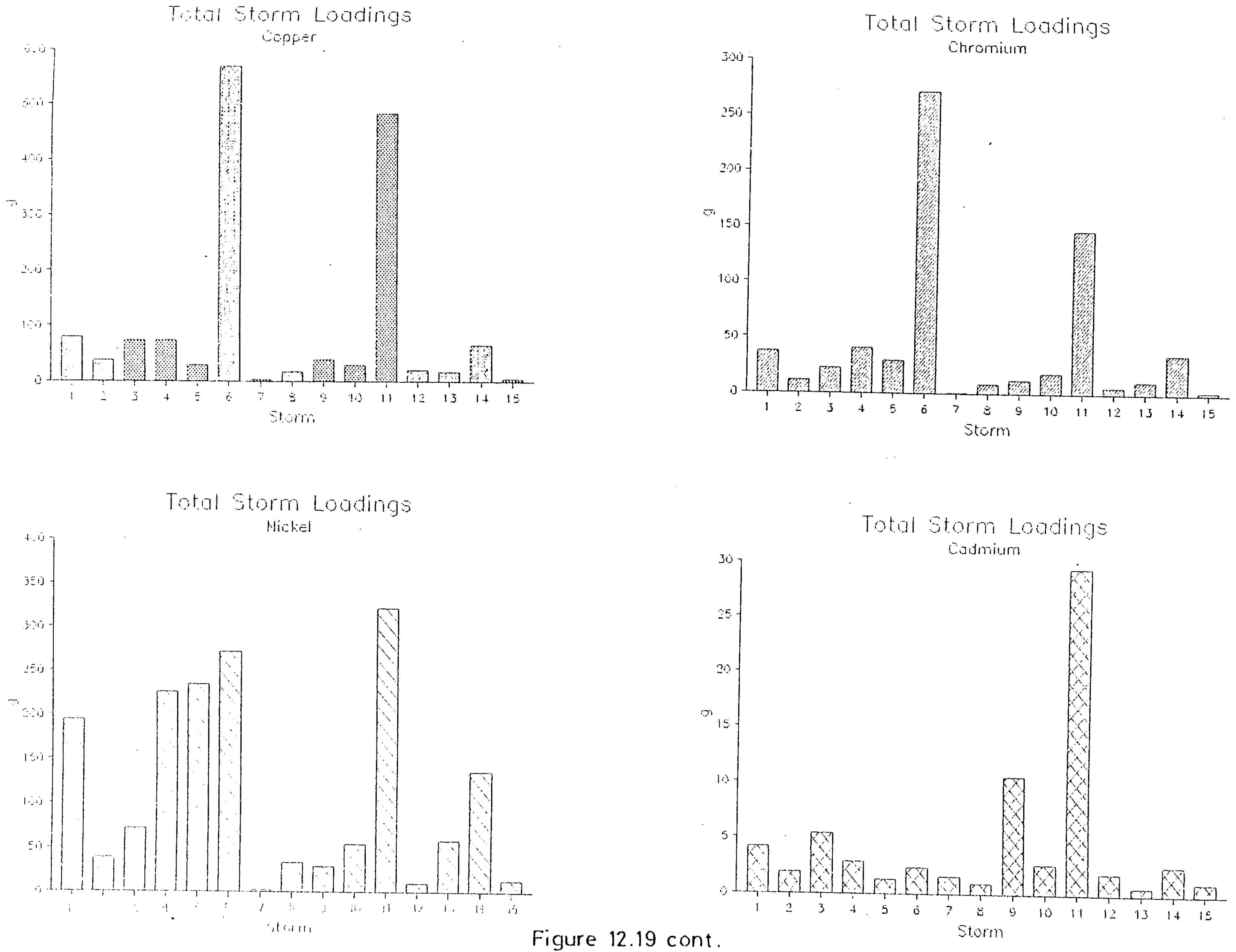


Figure 12.19 cont.

f) the composition of the storm sewer network,

and g) the general effectiveness of waste removal.

It is therefore difficult to carry out a direct comparison of the heavy metal loadings produced by only one storm with those of another storm within a different catchment. Even within specific areas the loadings can display considerable variation due to a large number of contributing factors, such as those listed above.

12.6.3 Correlation Matrices

In order to assess how the parameters, such as rainfall intensity and flowrate, may have influenced the total heavy metal loads produced, correlation matrices between the individual total metal loads and various meteorological and hydrological parameters were computed. Table 12.11 describes the meteorological and hydrological information relating to each storm event, this Table is also represented graphically in Figure 12.20. Table 12.12 presents data relating to the rainfall events prior to the one producing the sampled runoff. This has been included in an attempt to take into account antecedent storm conditions. Also included in the analyses were the total flow weighted mean metal concentrations (see Section 12.5.1) and the number of days since the last street cleansing event.

Table 12.13 highlights the various parameters between which good correlations were found (i.e. $r = 0.8 - 0.99$) and Table 12.14 presents those for which the correlations were reasonably good (i.e. $r = 0.6 - 0.8$).

STORM	R/F TOTAL mm	R/F MAX mm/hr	R/F MEAN mm/hr	STORM DURAT mins	FLOW TOTAL l	DISCH MAX l/sec	DISCH MEAN l/sec	HYDRO DURAT mins
1	1.8	6	2.17	92	389412	206.25	142.60	45
2	1.8	24	14.40	14	538114	586.25	224.49	38
3	4.8	6	2.97	164	2459718	531.25	247.23	109
4	1.6	24	13.00	8	522090	493.75	256.70	37
5	1.2	12	3.36	86	491122	218.75	161.75	50
6	4.8	6	1.67	236	1706069	446.82	192.82	166
7	0.8	1	0.72	54	93520	90.00	81.83	19
8	1.4	6	2.78	34	411382	356.16	352.07	19
9	8.4	3	1.62	362	1619284	261.46	186.79	144
10	2.8	3	1.18	150	1045437	140.00	121.97	142
11	7.4	48	11.58	98	3169893	2012.54	623.89	91
12	3.6	3	1.26	166	813306	261.46	167.46	17
13	1.4	12	6.60	12	120162	140.00	100.44	20
14	2.2	18	9.24	20	484792	588.83	290.71	28
15	1.2	12	5.75	14	233964	200.00	159.98	24

Table 12.11 Data relating to stormwater analysis.

Key: R/F mm - rainfall
R/F mm/hr - rainfall intensity
DURA - duration
DISCH - discharge
HYDRO - hydrograph

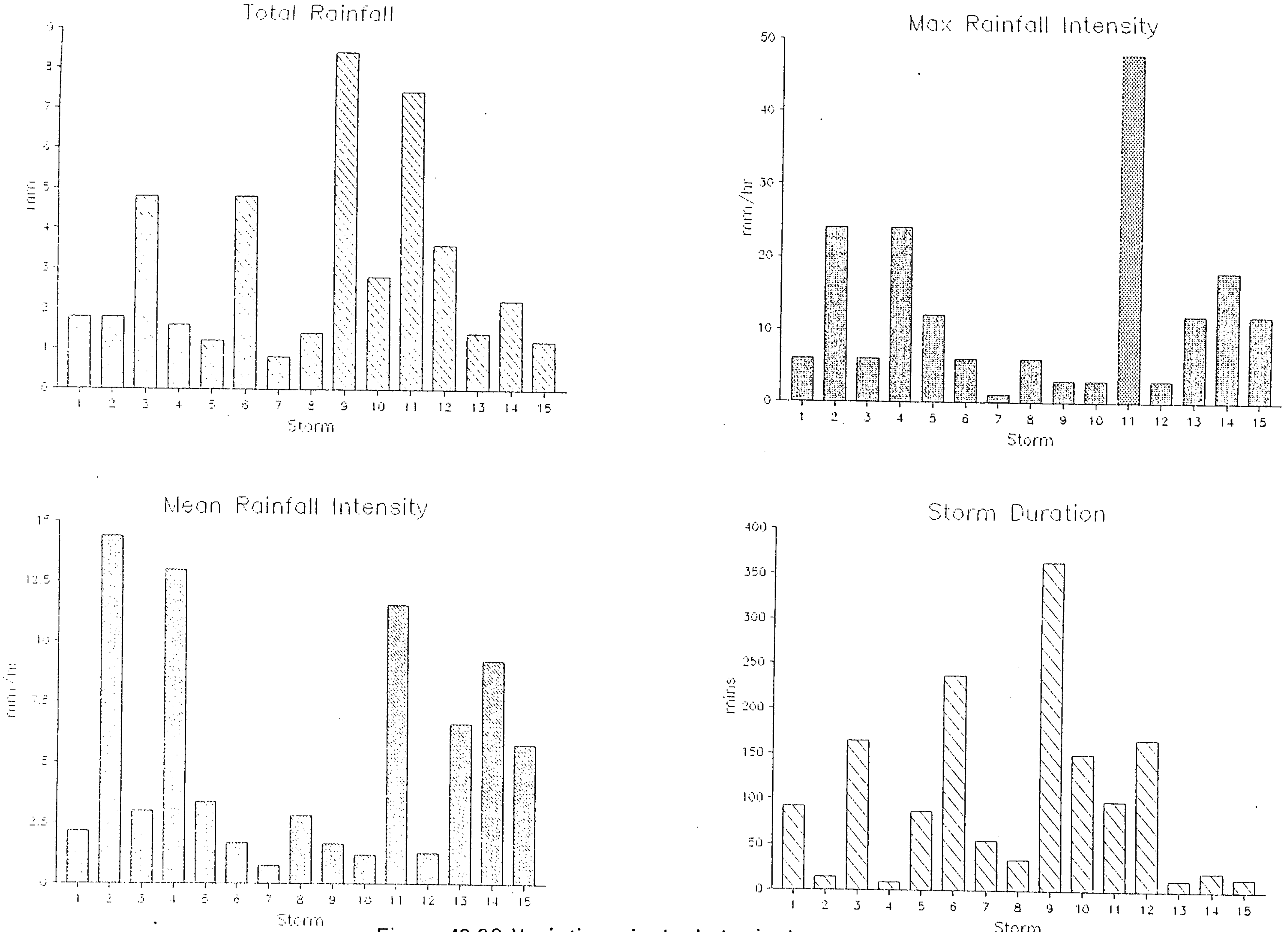


Figure 12.20 Variations in hydrological parameters.

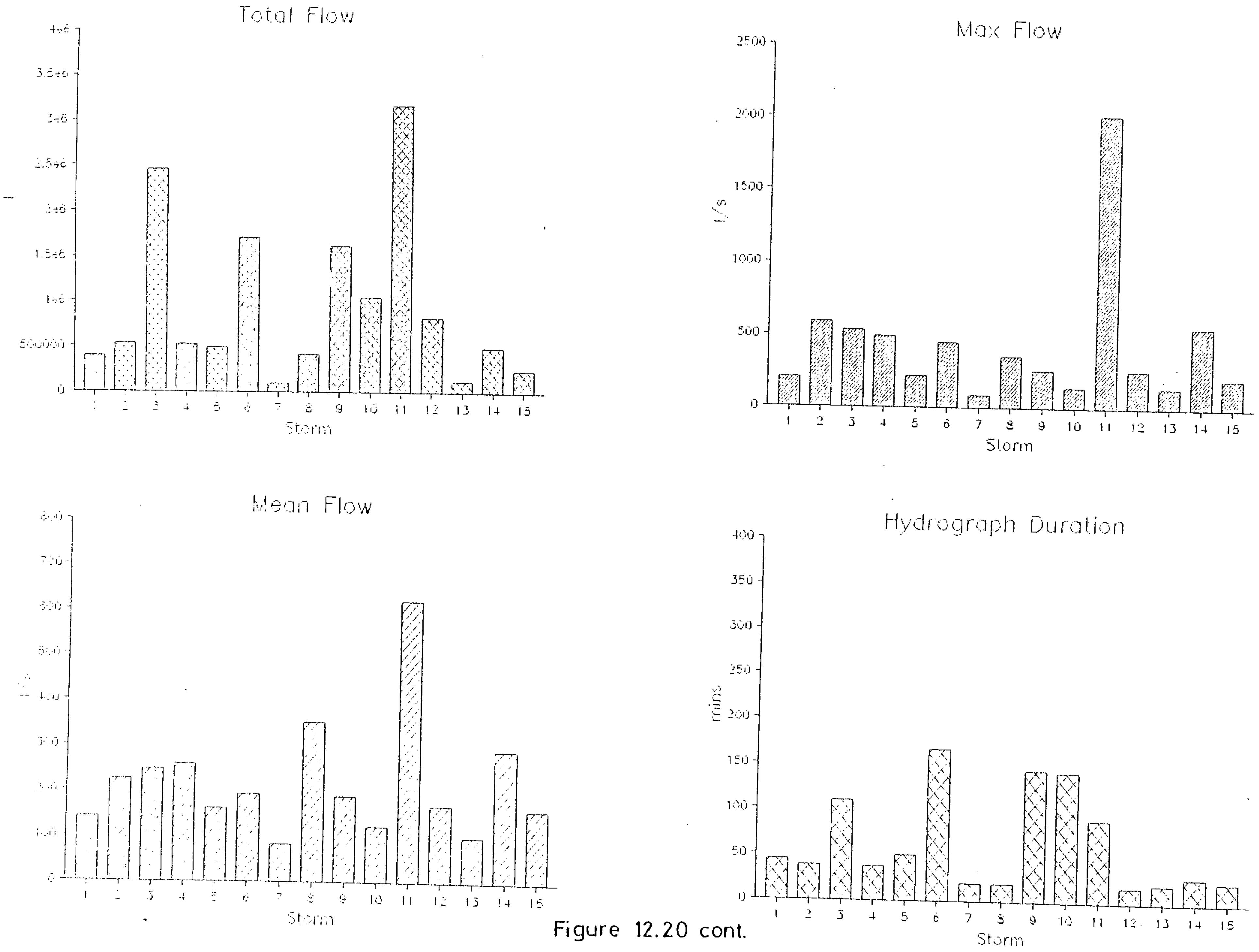


Figure 12.20 cont.

STORM	RAINFALL (R/F a) PRIOR TO SAMPLING EVENT					STREET CLEAN PRIOR days
	R/F TOTAL mm	R/F MAX mm/hr	R/F MEAN mm/hr	R/F DURATION mins	PRIOR TO EVENT mins	
1	1.0	6.0	3.60	28	144	13
2	0.4	2.0	1.15	6	582	3
3	0.8	1.2	0.85	34	950	13
4	0.4	1.0	0.50	12	4058	7
5	1.6	24.0	13.00	8	404	-
6	0.4	0.5	0.25	24	1656	8
7	9.4	3.0	1.64	372	2950	2
8	0.8	1.0	0.72	54	404	-
9	5.8	18.0	4.16	276	1230	2
10	0.6	3.0	1.30	24	8575	4
11	13.8	6.0	2.00	514	3720	2
12	0.4	0.8	0.37	16	618	-
13	0.4	2.0	1.07	6	900	1
14	1.4	12.0	6.60	12	142	-
15	6.6	18.0	5.45	114	970	12

Table 12.12 (a) Rainfall and street cleaning prior to sampling event.

Key: R/F mm - total rainfall
R/F mm/hr - rainfall intensity

RAINFALL (R/F b) PRIOR TO PREVIOUS RAINFALL (R/F a)					
STORM	R/F TOTAL mm	R/F MAX mm/hr	R/F MEAN mm/hr	R/F DURATION mins	PRIOR TO EVENT mins
1	3.6	30.0	10.00	24	20390
2	1.0	2.0	1.30	33	74
3	0.8	1.2	0.63	58	264
4	0.8	0.9	0.61	64	2988
5	0.4	1.0	0.50	12	4058
6	0.4	0.6	0.30	20	11492
7	1.2	1.5	0.81	86	120
8	9.4	3.0	1.64	372	2950
9	0.4	0.5	0.28	22	9122
10	7.6	6.0	2.46	226	263
11	0.8	3.0	1.10	44	1354
12	7.4	48.0	11.58	98	1186
13	1.0	1.0	0.92	54	8774
14	0.4	2.0	1.07	6	900
15	1.8	1.5	1.14	100	990

Table 12.12 (b) Rainfall prior to previous rainfall.

Key: R/F mm - total rainfall
R/F mm/hr - rainfall intensity

TOTAL STORM LOADS		FLOW WEIGHTED MEAN CONC.	
Correlation	Correlation Coefficient	Correlation	Correlation Coefficient
Fe : Pb	0.98	Peak total metal	
: Zn	0.95	: Fe	0.96
: Cd	0.90	: Cu	0.86
: Total metal	0.99	: Cr	0.80
: Max r/f intensity	0.87	: Total metal	0.92
: Max flow	0.95		
: Total flow	0.95	Fe : Pb	0.90
: Mean flow	0.86	: Cu	0.88
		: Total metal	0.99
Pb : Zn	0.98		
: Cd	0.94	Pb : Cu	0.89
: Total metal	0.98	: Total metal	0.95
: Max r/f intensity	0.81		
: Max flow	0.96	Cu : Cr	0.87
: Man flow	0.87	: Total metal	0.92
Zn : Cd	0.94	HYDROLOGIC PARAMETERS	
: Total metal	0.90		
: Max flow	0.94	Total rainfall	
: Mean flow	0.84	: Total flow	0.86
Cu : Cr	0.97	Max r/f intensity	
		: Max flow	0.88
Cd : Total metal	0.91		
: Max flow	0.89	Max flow	
		: Mean flow	0.93
Total metal			
: Max r/f intensity	0.86	Total rainfall a	
: Max flow	0.95	: Duration a	0.96
: Mean flow	0.86		
		Max r/f intensity a	
		: Mean r/f intensity a	0.91
		Max r/f intensity b	
		: Mean r/f intensity b	0.98
		Total rainfall b	
		: Duration b	0.85

Table 12.13 Stormwater correlation coefficients (r = 0.80-0.99).

Key: a - rainfall event prior to the sampled event
b - rainfall event prior to event a

TOTAL STORM LOADS		FLOW WEIGHTED MEAN CONC.	
Correlation	Correlation Coefficient	Correlation	Correlation Coefficient
Fe : Ni	0.63	Peak total metal	
: Cu	0.65	: Pb	0.78
: Total flow	0.67		
: Total rainfall a	0.66	Fe : Cr	0.77
: Duration a	0.63	: Max r/f intensity	0.71
		: Mean r/f intensity	0.73
Pb : Cu	0.71		
: Ni	0.63	Pb : Zn	0.72
: Total flow	0.75	: Cr	0.67
: Total rainfall a	0.66	: Max r/f intensity	0.79
: Duration a	0.67	: Mean r/f intensity	0.62
		: Max flow	0.73
Zn : Cu	0.69	: Mean flow	0.70
: Max r/f intensity	0.77		
: Total flow	0.74	Zn : Cu	0.78
: Total rainfall a	0.66	: Cd	0.62
: Duration a	0.66	: Total metal	0.61
Cr : Ni	0.73	Cr : Ni	0.73
		: Total metal	0.77
Ni : Total metal	0.64		
		Total metal	
Cd : Total rainfall	0.74	: Max r/f intensity	0.76
: Max r/f intensity	0.70		
: Total flow	0.79	HYDROLOGIC PARAMETERS	
: Mean flow	0.79		
: Total rainfall a	0.73	Total rainfall	
: Duration a	0.77	: Storm duration	0.79
Total metal		Max r/f intensity	
: Total flow	0.69	: Mean flow	0.79
: Total rainfall b	0.66		
: Duration b	0.63	Storm duration	
		: Hydrograph duration	0.79
		Total flow	
		: Max flow	0.73
		: Mean flow	0.65
		: Hydrograph duration	0.68

Table 12.14 Stormwater correlation coefficients (r = 0.60-0.80).

Key: a - rainfall event prior to the sampled event
b - rainfall event prior to event a

As would probably be expected from consideration of the individual storm concentration correlations (Section 12.4), the total metal loadings and the total flow weighted mean concentrations were all well related to one another (e.g total loadings of iron to those of lead had a correlation coefficient of 0.98, and for the flow weighted mean concentration between iron and lead the value was 0.9).

The majority of metal loadings were well correlated to the maximum, mean and total flow, suggesting that the greater the volume and rate of runoff the greater was the quantity of heavy metal pollutants discharged.

The heavy metal loadings were also seen to be closely correlated with the maximum intensity of the rainfall event producing the runoff. This suggested that the greater the rainfall intensity, the greater is the removal of surface contaminants, which agrees with the findings of Sartor and Boyd (1972). Cadmium was the only metal which was found to be correlated with the total amount of rainfall, which probably reflected the greater solubility of cadmium when compared with that of the other metals.

The total metal, iron, lead, zinc and cadmium loads were reasonably well related to the total rainfall and the rainfall duration of the previous event. By correlating the metals with the previous event, consideration is indirectly taken of the antecedent dry period and the corresponding build up of contaminants. Since the total metal loads for the storms under analysis were all well correlated with the previous rainfall it would appear that the rainfall from that storm had washed the build up of contaminants from the surface and the accumulation of metals during the antecececedent dry period was directly related to the loads discharged. However, a number of factors will contribute to this and make any direct comparisons virtually impossible.

There appeared to be no significant correlations between the parameters pertaining to the rainfall events prior to the one before the sampled event, indicating that the effects of the immediately previous event masked the effects of those before that event.

The flow weighted mean concentrations again appeared to be well correlated with one another and some significant correlations were observed between them, namely for the flow and rainfall for the specific rainfall runoff event. No significant correlations were seen to occur for the previous rainfall events, as the flow weighted mean concentrations were specific to a particular storm.

The peak total metal concentrations tended to be well correlated with the flow weighted mean concentrations. Since the peak concentrations varied with the flow weighted averages, any change within the peak metal concentrations would therefore effect the flow weighted mean concentrations.

As would be expected, some significant correlations were observed between the hydrologic parameters. These included total rainfall and total flow ($r = 0.86$), the maximum rainfall intensity and maximum flow ($r = 0.88$), the total rainfall and storm duration ($r = 0.96$), and between the maximum flow and mean flow, total flow to maximum flow, mean flow and hydrograph duration and between storm duration and hydrograph duration, for the latter see Figure 12.21. From consideration of the Figure it can be seen that there were two relationships, that of the hydrograph duration greater than the storm duration and vice versa.

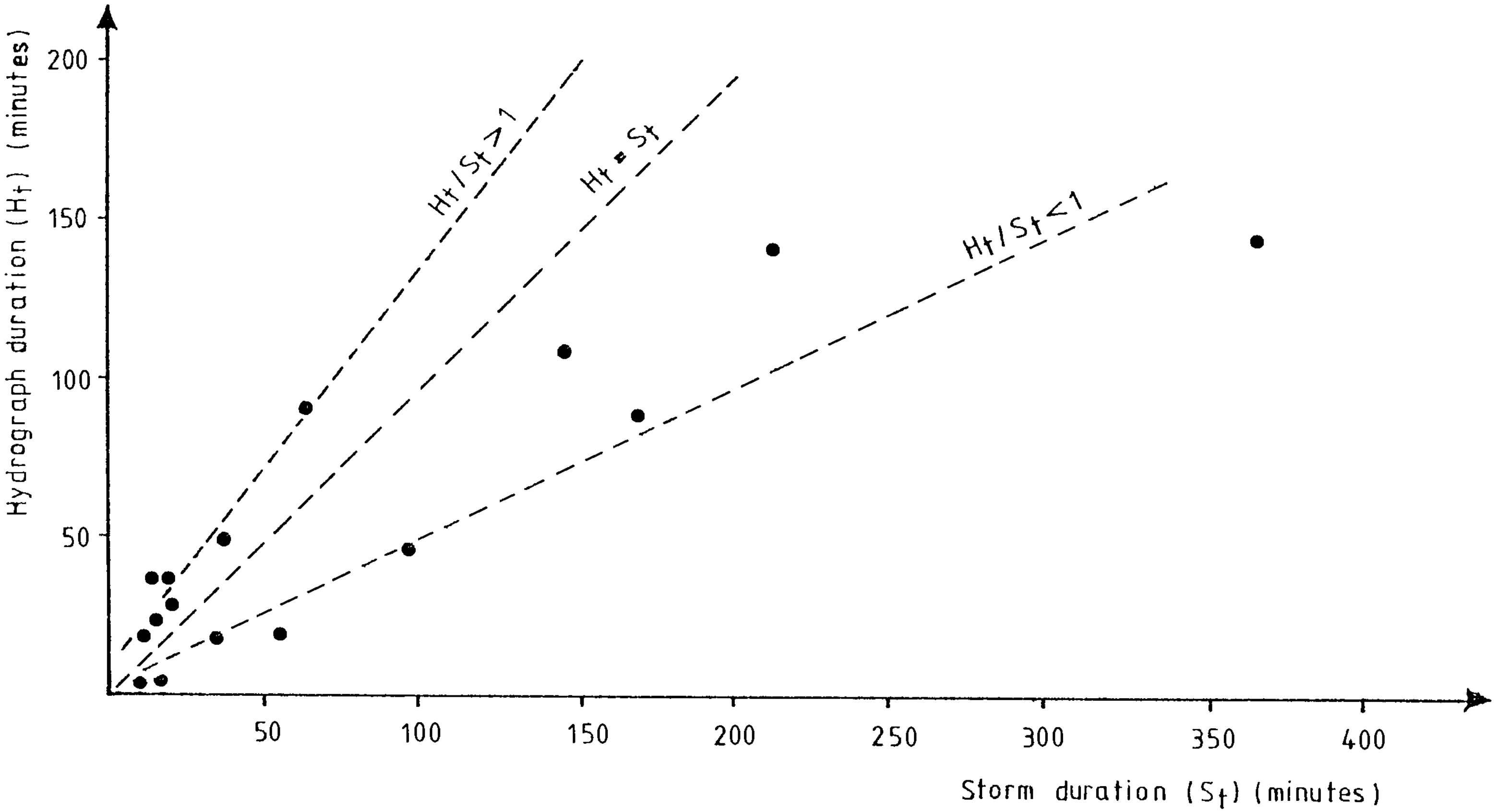


Figure 12.21 Graph illustrating two distinct patterns in relationship between hydrograph duration and storm duration.

12.6.3.1 Discussion

The majority of the metal loadings and the flow weighted mean concentrations were well correlated . This was also found to be the case within the individual stormwater concentrations.

The flow weighted mean concentrations tended to only exhibit significant correlation with the rainfall runoff sampled, whereas the total metal loadings were not only well correlated to the current rainfall event but to a lesser extent, also correlated well with the rainfall characteristics of the immediately previous event.

The total metal loads were well correlated with the total volume of flow. This relationship has also been found by a number of researchers including Whipple et al (1978), Bourcier and Sharma (1980), Mance (1981) and Ellis (1982). The total mass loads were also observed to be well correlated with the maximum and mean flowrates, again relationships which had previously been observed (Harrop (1984)). Pope et al (1978), however, stressed that it was the maximum runoff intensity rather than the runoff volume which was the major influence on the mechanism of removal of contaminants from road surfaces. The maximum metal concentrations were also found to be closely related to the flow weighted mean concentrations, which agreed with the findings of Mance (1981) for the Shephall catchment.

A number of authors have observed that the rainfall volume correlated well with the contaminant loadings (Harrop (1984), Waller (1972), Pope (1980), AVCO (1970) and Adams (1978)). Such a relationship was not found to exist for the metals analysed in this study apart from cadmium. However, a relationship was found to exist between the maximum rainfall intensity and the metal loadings and both

Reinertsen (1981) and Pratt and Adams (1981 and 1984) consider that runoff loadings are availability limited functions, with initial rainfall intensity being important for particle and pollutant removal.

The hydrologic parameters were well correlated with one another for each specific event.

As no significant relationships between the number of days since street cleaning and metal concentrations were found, street cleansing events appeared to make little contribution to the total storm loadings observed in this particular aspect of the analysis.

It should be noted at this point, that only the total metal storm loads were used in the computations and differences may be expected if the particulate and soluble metals were studied individually.

12.6.4 Metal Proportions

The relative proportions of individual metals, with respect to the total metals discharged during each storm were calculated and expressed as a percentage. The results are presented in Table 12.15. From consideration of the Table it can be seen that the proportions of each metal vary, both between the soluble and particulate phase and between storm events. Iron was the predominant metal in all phases, with the particulate metal phase having the highest mean percentage of 96% and ranging between 92 and 98%. The mean value for the soluble iron was approximately 60%. Since iron was the predominant metal the calculations were repeated excluding iron from the total and the results are given in Table 12.16.

STORM		IRON	LEAD	ZINC	COPPER	CHROMIUM	NICKEL	CADMIUM
1	P	95.65	1.41	1.14	0.81	0.56	0.08	0.009
	S	71.26	7.69	11.37	2.22	0.95	6.36	0.130
	T	79.20	5.56	8.15	1.76	0.82	4.32	0.092
2	P	95.72	1.51	1.81	0.40	0.34	0.22	0.013
	S	55.73	18.75	15.34	4.17	0.50	5.16	0.240
	T	87.20	5.19	4.70	1.22	0.37	1.28	0.036
3	P	96.94	1.20	0.74	0.25	0.58	0.13	0.155
	S	76.91	9.86	7.97	2.34	0.48	2.33	0.107
	T	83.27	7.11	5.67	1.68	0.51	1.63	0.122
4	P	97.17	1.68	0.07	0.62	0.27	0.17	0.009
	S	73.36	13.25	0.45	1.52	1.05	10.26	0.100
	T	91.65	4.36	0.16	0.83	0.45	2.52	0.032
5	P	97.06	0.81	0.04	0.26	1.02	0.74	0.050
	S	52.43	9.75	0.17	3.67	3.05	30.79	0.012
	T	73.01	5.63	0.11	2.09	2.12	16.94	0.091
6	P	95.36	1.79	1.26	0.88	0.65	0.08	0.011
	S	52.55	12.07	8.25	13.81	6.42	6.85	0.050
	T	70.60	7.74	5.30	8.36	3.99	4.00	0.030
7	P	97.88	0.14	0.71	0.28	0.61	-	0.370
	S	60.69	23.16	5.12	4.01	0.52	4.34	2.130
	T	75.23	14.27	3.42	2.57	0.56	2.66	1.450
8	P	96.92	1.19	1.15	0.27	0.44	0.03	0.006
	S	53.64	27.15	9.05	2.67	0.63	6.68	0.170
	T	84.19	8.82	3.47	0.97	0.49	1.98	0.054
9	P	91.70	1.54	2.30	1.08	1.64	1.05	0.670
	S	61.82	18.91	12.95	3.02	0.46	2.15	0.680
	T	69.58	14.40	10.18	2.52	0.77	1.87	0.680
10	P	96.93	1.01	1.28	0.20	0.35	0.18	0.026
	S	59.38	20.82	10.96	2.54	1.05	5.04	0.220
	T	84.89	7.36	4.39	0.95	0.58	1.74	0.087
11	P	93.50	2.87	1.92	0.95	0.43	0.30	0.026
	S	64.00	17.98	13.87	1.82	0.23	1.90	0.178
	T	84.12	7.67	5.72	1.22	0.37	0.81	0.074

Table continued overleaf

STORM		IRON	LEAD	ZINC	COPPER	CHROMIUM	NICKEL	CADMIUM
12	P	97.00	0.01	1.02	0.37	0.97	0.33	0.130
	S	48.24	14.48	27.23	6.08	0.79	2.75	0.430
	T	74.48	6.72	13.16	3.02	6.89	1.45	0.270
13	P	95.97	1.09	1.02	0.85	0.18	0.16	0.050
	S	65.23	9.47	9.87	2.38	1.47	11.50	0.087
	T	80.59	5.29	5.46	1.62	1.10	5.86	0.070
14	P	96.29	1.10	1.34	0.47	0.51	0.26	0.009
	S	62.42	13.98	13.87	2.40	0.78	6.42	0.011
	T	84.95	5.42	5.54	1.11	0.60	2.33	0.045
15	P	99.18	0.38	0.21	0.07	0.04	0.10	0.002
	S	42.85	20.14	25.76	1.79	0.06	8.32	1.060
	T	98.38	0.70	0.58	0.09	0.04	0.22	0.018
Mean	P	96.22	1.19	1.09	0.52	0.57	0.25	0.102
	S	60.03	15.83	11.48	3.63	1.23	7.39	0.390
	T	81.42	7.08	5.07	2.00	1.31	3.31	0.212

Table 12.15 Total storm load proportions including iron.

Key: P = Particulate metal
S = Soluble metal
T = Total metal

STORM		LEAD	ZINC	COPPER	CHROMIUM	NICKEL	CADMIUM
1	P	32.47	33.73	18.67	12.90	1.86	0.22
	S	26.77	39.60	7.72	3.29	22.14	0.46
	T	27.14	39.18	8.46	3.95	20.76	0.44
2	P	35.23	42.33	9.29	7.91	5.23	0.32
	S	42.37	34.66	9.63	1.13	11.66	0.55
	T	40.56	36.73	9.56	2.91	9.99	0.49
3	P	39.19	24.26	8.28	19.07	4.20	5.07
	S	42.70	34.53	10.13	2.08	10.09	0.46
	T	42.49	33.94	10.03	3.07	9.75	0.73
4	P	59.49	2.46	21.99	9.56	6.16	0.34
	S	49.70	1.69	5.69	3.97	38.54	0.39
	T	52.27	1.90	9.93	5.42	30.17	0.38
5	P	27.69	1.38	8.80	34.85	25.35	1.73
	S	20.49	0.35	7.72	6.42	64.74	0.26
	T	20.86	0.41	7.78	7.85	62.79	0.34
6	P	38.70	27.07	18.90	13.95	1.82	0.25
	S	24.43	17.38	29.11	13.53	14.44	0.10
	T	26.31	18.02	28.43	13.56	13.60	0.11
7	P	6.44	33.44	13.20	28.88	-	17.50
	S	58.94	13.03	10.21	1.34	11.63	5.43
	T	57.63	13.81	10.37	2.27	10.75	5.87
8	P	38.96	37.56	8.69	14.29	0.98	0.18
	S	58.58	19.52	5.77	1.36	14.42	0.37
	T	55.81	21.98	6.17	3.13	12.56	0.34
9	P	18.53	27.76	13.09	19.82	12.64	8.12
	S	49.52	33.92	7.91	1.21	5.64	1.80
	T	47.36	33.49	8.28	2.53	6.14	2.25
10	P	32.93	14.74	6.49	11.56	5.95	0.85
	S	51.25	26.97	6.26	2.58	12.40	0.53
	T	48.76	29.03	6.29	3.82	11.52	0.57
11	P	44.17	29.49	14.56	6.67	4.71	0.39
	S	49.96	38.56	5.05	0.64	5.29	0.49
	T	48.33	36.03	7.71	2.33	5.13	0.47

Table continued overleaf

STORM		LEAD	ZINC	COPPER	CHROMIUM	NICKEL	CADMIUM
12	P	0.54	35.85	13.11	34.01	11.74	4.73
	S	27.98	52.60	11.75	1.54	5.32	0.83
	T	26.32	51.60	11.83	3.49	5.70	1.06
13	P	27.08	25.33	21.16	17.82	3.94	1.32
	S	27.24	28.39	6.84	4.23	33.10	0.25
	T	27.30	28.16	8.34	5.65	30.18	0.36
14	P	29.75	36.12	12.58	13.78	7.13	0.26
	S	37.22	36.91	6.39	2.08	17.08	0.31
	T	36.02	36.81	7.41	4.00	15.46	0.30
15	P	47.79	26.42	8.36	5.09	13.17	0.28
	S	35.25	45.10	3.13	0.11	14.55	1.86
	T	41.30	35.89	5.67	2.54	13.85	1.09
Mean	P	31.93	28.32	13.14	16.68	6.99	2.77
	S	40.22	28.21	8.88	3.03	18.74	0.94
	T	39.89	27.80	9.75	4.43	17.22	0.99

Table 12.16 Total storm load proportions excluding iron.

Key: P = Particulate metal
S = Soluble metal
T = Total metal

When non-ferrous metals were considered lead and zinc were found to predominate. There was to be no great variation between the mean zinc percentages for both the particulate and soluble phases, the average value being approximately 28%.

There were notable variations between the particulate and soluble metal loadings for each storm. Taking account of the mean values, for lead and nickel percentages, there was generally a higher proportion of the metal within the soluble phase than in the particulate phase, whereas for zinc, copper, chromium and cadmium a greater proportion occurred within the particulate phase.

The mean metal percentages computed for the total storm loads were comparable with those obtained for the individual storm events (Section 12.3).

12.6.5 Total Storm Loads Including Assumed Boundaries

In order to estimate the total metal loadings for an entire storm event and not only during the sampling period, it was necessary to take into account the start and tail of the hydrograph. Thus in calculating the total metal loadings corresponding to the start and finish of the storm assumptions had to be made, as the time history of concentration and flow for those periods were unknown entities. Generally, flow and metal concentration levels were known for the first three minute interval of the sampling period and similarly they were known twelve minutes from the end. For ease of calculation, it was therefore assumed that the values of metal concentration and flow were at baseflow levels at both the start and end of the sampling period. Hence, the concentration levels and flow at the start of the storm were half the values occurring at three minutes into the period.

A similar assumption was made for the end of the period.

The revised total metal loadings are given in Table 12.17. The values were used in the modelling study discussed in Chapter 14.

12.7 Mass of the First Flush

Using the data obtained from the total storm load calculations, graphs based on the technique by Tucker (1975) were drawn to enable the mass of the first flush to be determined (see Section 3.3). Briefly this required the analysis of each individual event and the cumulative mass discharge (instantaneous concentration multiplied by flow) to be plotted against and the cumulative square of flow. A typical curve of this type is shown in Figure 12.22.

Characteristically for those graphs the slope is initially high, corresponding to the first flush phase, and then falls to a nearly constant value corresponding to the subsequent phase (Tucker and Mortimer (1978)). The mass of the first flush is obtained by projecting a line from the line corresponding to the subsequent phase, the point at which the line intersects the y axis gives the mass of the first flush.

Plots were drawn for the total metal concentrations in all three phases (i.e. particulate, soluble and total), for all of the fifteen storm events sampled. Total metal concentration was used to give an indication of the total metal mass of the first flush, an example of which is shown in Figure 12.23.

STORM		IRON	LEAD	ZINC	COPPER	CHROMIUM	NICKEL	CADMIUM	TOTAL
1	P	1433	20.96	21.82	12.11	8.77	1.18	0.14	1498
	S	2244	244	346	70.88	31.11	224	6.01	3166
	T	3677	265	368	82.99	39.88	225	6.16	4664
2	P	2347	36.81	44.43	9.73	8.39	5.48	0.34	2452
	S	376	127	105	28.49	3.29	34.14	1.64	676
	T	2723	164	150	38.22	11.68	39.62	1.98	3128
3	P	1390	17.18	10.63	3.64	8.40	1.88	2.19	1433
	S	2357	305	241	72.46	14.87	71.46	3.30	3064
	T	3747	322	251	76.10	23.27	73.34	5.49	4498
4	P	6960	123	4.92	45.60	19.45	12.52	0.73	7167
	S	1615	276	9.89	35.33	24.52	235	2.22	2197
	T	8575	398	14.81	80.93	43.97	247	2.95	9364
5	P	634	5.37	0.26	1.67	6.76	4.98	0.34	653
	S	402	74.79	1.35	28.13	24.11	244	0.95	776
	T	1036	80.16	1.61	29.80	30.87	249	1.29	1429
6	P	2869	55.56	38.07	27.04	19.35	2.42	0.34	3012
	S	2183	496	342	547	254	281	2.04	4105
	T	5052	552	380	574	273	283	2.38	7117
7	P	46.68	0.08	0.32	0.13	0.27	-	0.16	47.63
	S	46.78	18.17	3.74	3.09	0.54	3.42	1.58	77.30
	T	93.46	18.25	4.05	3.22	0.81	3.42	1.75	125
8	P	1351	16.49	15.90	3.72	5.90	0.36	0.09	1394
	S	74	157	52.02	15.69	4.30	41.09	1.20	346
	T	1426	174	67.92	19.41	10.20	41.45	1.29	1740
9	P	367	6.16	9.23	4.35	6.59	4.42	2.70	401
	S	707	216	148	34.53	5.28	24.64	7.87	1144
	T	1074	222	157	38.89	11.87	28.84	10.56	1544
10	P	2050	21.40	27.13	4.22	7.51	3.87	0.55	2115
	S	593	208	109	25.40	10.46	50.36	2.16	999
	T	2643	229	136	29.62	17.97	54.22	2.71	3114
11	P	26558	834	543	275	124	87.09	7.41	28428
	S	8591	2382	1838	236	30.66	251	23.71	13353
	T	35149	3216	2282	511	154	338	31.12	41781
12	P	376	0.09	4.05	1.45	3.68	1.32	0.54	387
	S	163	49.04	91.29	20.37	2.68	9.24	1.45	337
	T	539	49.12	95.34	21.82	6.35	10.56	1.99	724

Table continued overleaf

STORM		IRON	LEAD	ZINC	COPPER	CHROMIUM	NICKEL	CADMIUM	TOTAL
13	P	550	6.60	5.99	4.90	4.14	0.87	0.27	573
	S	372	54.49	56.65	13.23	8.64	57.71	0.44	563
	T	892	61.09	62.62	18.13	12.78	58.58	0.70	1136
14	P	4004	47.88	55.35	19.39	21.85	11.12	0.37	4160
	S	1335	295	292	50.57	16.31	135	2.46	2126
	T	5339	343	347	69.96	38.16	146	2.83	6286
15	P	5995	25.47	14.08	4.54	2.69	6.62	0.16	6048
	S	41.91	21.01	25.11	1.82	0.06	8.41	0.97	99.29
	T	6037	46.48	39.19	6.36	2.74	15.03	1.13	6147

Table 12.17 Calculated total storm loads for entire storm (g). (values are rounded values for ease of presentation)

Key: P = Particulate metal
S = Soluble metal
T = Total metal

Figure 12.22 Typical plot of $\sum(ISL)T$ against $\sum Q^2T$ for the calculation of the mass of the first flush.
(Tucker & Mortimer (1978))

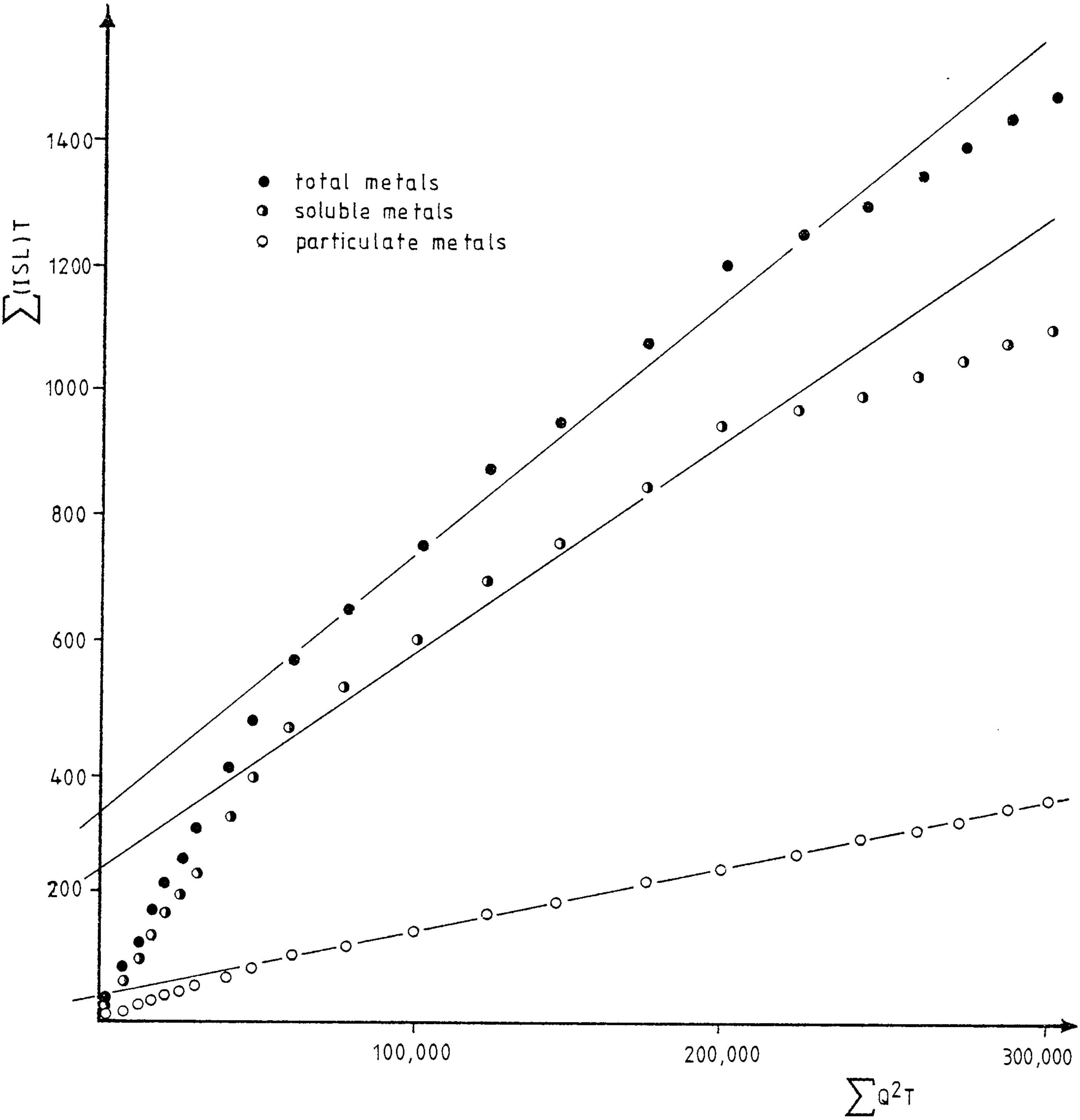


Figure 12.23 Calculation of the mass of the first flush for Storm 9 on 2/1/84.

Not all storm events displayed a first flush and in these instances the graphs did not show the pattern as described by Tucker, hence the mass of the first flush could not be calculated for each event in this manner. Some of the storms were either of too short or of too long a duration to obtain the general pattern, e.g. storm 6 (25/11/83) showed a number of distinct lines due to its long duration.

The storm events where the mass of the first flush could be identified in this manner are given in Table 12.18, where the mass is expressed as a percentage of the total storm load. From consideration of the Table it can be seen that where the mass of the first flush could be calculated, it accounted for between 20 and 40% of the total mass output of the storm.

As the first flush was not a constant feature of all runoff events it was deemed necessary to calculate the percentage of pollutants discharged during each time interval and this will be discussed in the next Section.

12.8 Cumulative Metal Percentages

The proportion of each metal relative to the total mass of metals discharged were calculated for each storm event and the results, expressed as a percentage, will now be briefly discussed.

STORM	PERCETAGES		
	Total	TOTAL METALS Particulate	Soluble
5 (03/11/83)	21	21	34
9 (02/01/84)	21.5	12	22
10 (22/01/84)	28	38	22
12 (25/05/84)	34.5	41	31
15 (15/07/84)	26	29	19

Table 12.18 Mass of the first flush.
(expressed as percentage of total mass discharged)

12.8.1 Storm 1 (16/08/83)

Approximately 50% of all the metals were discharged within the first 15 minutes i.e. in one third of the storm duration time. However, there was seen to be a slight variation between the individual metal species, some of the metals were slightly lower than this e.g. particulate cadmium (24%), whilst some were higher (particulate nickel 65%). By the time 30 minutes had passed, between 85 and 90% of all metals had been discharged.

12.8.2 Storm 2 (16/09/83)

The storm duration was of 42 minutes and within the first 12 minutes approximately 50% of all the particulate metals had been discharged, with lead and copper reaching 62% at this time. Greater variation was seen with the soluble metal loads when compared with the particulate species, with the majority of metals reaching the 50% discharge point at a slightly later time of 15 minutes. Over 80% of all the particulate metals were discharged after a time of 21 minutes. The 80% value for the soluble metals was reached at a slightly later time of 26 minutes.

12.8.3 Storm 3 (10/10/83)

This was a very long storm with a duration of 173 minutes. Approximately 50% of the majority of metals, both particulate and soluble were discharged after a time of 110 minutes. After 148 minutes, only 25 minutes from the end of the storm, 90% of the majority of metals had been discharged. However, particulate cadmium loads were at a lower percentage at this time (64%) and only reached 90% after a time of 161 minutes.

12.8.4 Storm 4 (02/11/83)

Storm 4 was a fairly short storm of 41 minutes duration, with approximately 45 to 50% of the particulate metals being discharged after a time of 13 minutes. Generally, higher percentages of the soluble metals were discharged during this time, with soluble chromium reaching 70%. After 27 minutes into the storm, 90% of the majority of metals, both particulate and soluble had been discharged.

12.8.5 Storm 5 (03/11/83)

After 16 minutes into the storm (of duration 54 minutes) 45% of the total particulate metals had been discharged. However, the variations between the metals were quite considerable, and at this time ranged from 29% for particulate cadmium, to 69% for particulate chromium. Over 45% of all the soluble metals were discharged by this time, and hence higher percentages of soluble metals tended to be discharged earlier within the storm event when compared with their particulate counterparts. Approximately 90% of all metal species had been discharged by the time 35 minutes had passed.

12.8.6 Storm 6 (25/11/83)

Storm 6 was a long storm consisting of two parts with an overall duration of 170 minutes. There appeared to be a gradual increase in the discharge of metals over time. Only after a time of 139 minutes were 50% of the particulate metals discharged. The 50% level was reached for the soluble metals at a slightly earlier time of 132 minutes, with soluble chromium reaching 73% at this time. After a time of 157 minutes had passed 90% of all metals had been discharged.

12.8.7 Storm 7 (17/12/83)

Great variations were observed within the percentages of metals discharged in this short storm of 22 minutes duration. However, after a time of 13 minutes over 60% of the majority of particulate metals had been discharged, with the exception of chromium (53%) and Nickel (0%). Over 50% of the soluble metals were discharged within the first 10 minutes and by the time 13 minutes had passed between 50 and 70% of all soluble metals were discharged.

12.8.8 Storm 8 (17/12/83)

Approximately 50% of all metals, both soluble and particulate had been discharged within the first 13 minutes of the storm, just over half of the storm duration of 23 minutes. There were, however, variations between the metals e.g. 83.5% for particulate cadmium and 75% of the particulate nickel had been discharged at this time. Higher levels were also observed for their soluble counterparts.

12.8.9 Storm 9 (02/01/84)

The percentage of metals discharged with time varied quite considerably. Over 50% of the particulate nickel was discharged after a time of 16 minutes (storm duration being 148 minutes), by the time 48 minutes had passed 50% of the particulate lead had been discharged and by 79 minutes the particulate copper. Only 50% of the chromium loads had been discharged by a time of between 104 and 110 minutes. After a time of 92 minutes 50% of all other particulate metals were discharged.

The soluble metal percentages showed less variation than the particulate metals, with over 50% of iron, lead, zinc and copper being discharged after a time of 71 minutes and for chromium and nickel at a time of 79 minutes. Once again, the percentage discharge of cadmium occurred slightly later, with only 50% being discharged after a time of 117 minutes.

There tended to be a gradual increase in the percentage of metals discharged throughout the duration of the storm.

12.8.10 Storm 10 (22/01/84)

Less variation was observed between the metals during this event compared with previous events and this may have been due to the fact that the runoff event was produced by snowmelt.

Approximately 50% of all particulate metals, except for that of cadmium, were discharged during the first 69 minutes, the entire runoff period sampled was 149 minutes. Cadmium reached this level at a later time of 112 minutes. After a period of 131 minutes had elapsed, roughly 90% of all particulate metals had been discharged.

The soluble metals were discharged slightly later and 50% had been removed after a time of 75 minutes. As with the particulate metals over 90% of the majority of soluble metals were discharged by 131 minutes into the runoff period. However, cadmium once again was discharged slightly later, the 90% value being reached between 137 and 143 minutes.

12.8.11 Storm 11 (24/05/84)

This particular storm, of duration 96 minutes, displayed a totally different pattern to that of the other storms studied. Over 80% of all metals both particulate and soluble, were discharged within the first 21 minutes. The storm was characterized by extremely high flowrates producing a large volume of flow during the initial stages of the runoff. The metal concentrations were shown to be closely correlated with the flowrate and as the flowrate fell after a time of 30 minutes as did the metal loads.

12.8.12 Storm 12 (25/05/84)

Approximately 50% of the majority of metals, both particulate and soluble, were discharged during the first half of the storm i.e. after 42 minutes. There were a few exceptions to this and they included particulate nickel and soluble chromium, of which 50% was discharged after a time between 49 and 57 minutes.

12.8.13 Storm 13 (20/06/84)

As this was a very short storm of duration 24 minutes, it was difficult to distinguish any significant pattern. However, it did appear that 30% of the majority of particulate metals were discharged within the first 9 minutes.

The soluble metals tended to be discharged in greater quantities earlier than their particulate counterparts with over 60% of all metals being discharged after a time of 13 minutes. Cadmium once again displayed a different pattern, reaching only 41% after a period of 13 minutes.

12.8.14 Storm 14 (20/06/84)

This relatively short storm of 33 minutes displayed a large mass of metals discharged within a short period of time. Over 50% of all metals were discharged after a time of 9 minutes, with particulate chromium and cadmium exceeding 60%. After that time the metals proportions appeared to increase more gradually.

12.8.15 Storm 15 (15/07/84)

This was also a short storm of 28 minutes duration. Approximately 45 to 50% of all the particulate metals discharged within the first 8 minutes of the storm and over 50% of the soluble metals were discharged after a slightly later time of 12 minutes. Cadmium however, was discharged later during the storm.

12.8.16 Discussion

Each storm was unique and displayed different patterns, but some general observations were made.

During storms 5, 6, 13 and 14 there was a higher percentage of soluble metals discharged at an earlier stage than their particulate counterparts. This may simply be due to their ease of mobilization. They are transported through the system quicker than the particulate metals which have to be physically removed from the catchment surfaces before transportation. However, this trend was not evident in all storms and in certain cases (e.g. storm 15) the greater percentage of soluble metals were discharged later during the storm event.

The metals were often observed to follow similar discharge patterns and were discharged in similar relative amounts throughout an individual storm. Again this was not the case for all storms and during certain events, such as storms 5 and 9, great variation was seen to occur between the metals. This may have been due to their different origins, or their association with different particle size, being loaded onto the storm hydrograph at different times and in varying amounts.

During the storms of long duration there was usually a gradual increase in the percentage of metals discharged with time. This may have been due to low rainfall intensity causing slow mobilization of the metals. However, for the short duration storms, where only a few samples were taken, no general pattern was evident. In these cases the sampling period would determine, to a large extent, the calculated values of percentage of metals discharged with time.

In many of the storms, including storms 8, 10, 12 and 13, approximately 50% of the metals were discharged during the first half of the storm, whilst in others, 50% of the metals were discharged during only one third of the storms duration (e.g. storms 1, 2, 4 and 5). During storms 11 and 14 a large proportion of the metals were discharged within a very short period of time, thus suggesting the presence of a first flush.

Cadmium was frequently observed to be discharged later during the storm event and this could suggest that it is from a different source, being loaded onto the storm hydrograph at a later time than that of the other metals.

CHAPTER 13

PROPORTIONATE ANALYSIS

13.1 Metal Proportions

The metal proportions, expressed as percentages, were calculated for each data set and were given in the appropriate Chapters. The main reason for carrying out the proportionate analysis was to enable the comparison of all data sets since each were measured in different units i.e. deposit cannisters in total µg, road sediments and soils mg/kg and stormwater mg/l. The average values for the proportions are presented in Table 13.1. However, it should be noted that the values only represent mean values for the entire data sets and large variations were shown to exist between individual samples within the data sets both temporally and spatially.

From consideration of the Table it can be seen that great variation was exhibited within the data sets. Since iron was found to be the predominant metal within all groups of data, Table 13.2 was compiled excluding the iron content.

No close similarities were evident, apart from that of the topsoil and subsoil. The highest lead percentages were found within the road sediment samples, probably as a direct result of vehicular activity. High lead percentages were also observed within the deposited bank materials at the outfall of the sewer indicating contamination from the stormwater carrying lead, the lead being supplied by the road sediments (Payne (1985)). Zinc proportions were high within the soil samples indicating some local source of contamination which could have been from vehicle tyres or from local agricultural practices.

Since little information could be inferred from the results, a discriminant analysis was performed on the entire data.

METAL	PERCETAGES							
	ROAD SEDIMENT	DEPOSIT CANNISTER	TOPSOIL	SUBSOIL	STORMWATER			OUTFALL BANK
					P	S	T	
Fe	91.82	77.78	98.21	98.47	95.11	58.46	76.46	93.84
Pb	4.83	8.69	0.31	0.26	1.41	16.41	7.81	2.88
Zn	2.23	9.30	0.99	0.72	1.20	12.01	5.12	2.31
Cu	0.61	2.34	0.28	0.23	0.51	3.07	1.62	0.38
Cr	0.25	0.45	0.25	0.20	0.61	0.92	0.82	0.28
Ni	0.19	1.16	0.11	0.09	0.35	7.41	3.77	0.28
Cd	0.01	0.32	0.00	0.00	0.10	0.34	0.32	0.02

Table 13.1 Metal proportions including iron for all data.

Key: P = Particulate metal
S = Soluble metal
T = Total metal

METAL	PERCETAGES							
	ROAD SEDIMENT	DEPOSIT CANNISTER	TOPSOIL	SUBSOIL	STORMWATER			OUTFALL BANK
					P	S	T	
Pb	56.49	38.40	17.28	16.02	31.36	41.25	41.05	46.77
Zn	28.85	42.22	42.58	44.25	30.11	29.34	28.71	37.54
Cu	8.00	11.19	14.43	15.92	12.87	7.80	8.30	6.15
Cr	3.66	2.11	16.72	15.74	15.05	2.43	4.04	4.62
Ni	2.78	4.48	7.71	7.82	7.13	18.31	16.70	4.62
Cd	0.17	1.57	0.22	0.21	2.77	0.83	1.14	0.31

Table 13.2 Metal proportions excluding iron for all data.

Key: P = Particulate metal
S = Soluble metal
T = Total metal

13.2 Discriminant Analysis

Discriminant analysis was performed on the entire percentage data set using SPSS , Statistical Package for the Social Sciences. Through the application of discriminant analysis it was possible to calculate the effect of a collection of interval-level independent variables on a nominal dependent variable (classification). The result is a linear combination of independent variables that best distinguish the cases in the categories of the dependent variable.

Discriminant scores, the probability of membership in each category of the dependent variable and the predicted category was calculated.

Discriminant analysis begins with the desire to statistically distinguish between two or more groups of cases, in this case there were five, the number in each group are given in the first parentheses:

(i) SWS particulate stormwater metals (226), (group 1),
(ii) SWW soluble stormwater metals (226), (group 2),
(iii) RD road sediments (276), (group 3),
(iv) DP deposit cannisters (142), (group 4),
(v) SOIL soils (42), (group 5).

To distinguish between the groups it was necessary to select a collection of discriminating variables, that measure characteristics on which the groups were expected to differ, in this case metal percentages were used. The mathematical objective of discriminant analysis is to weight and linearly combine the discriminating variables in some fashion so that the groups are forced to be as statistically distinct as possible.

13.2.1 Results

Table 13.3 indicates the number of cases classified into each of the groups and the percent correct classification for each group.

From consideration of the Table it is evident that out of the possible 226 cases for the particulate stormwater metal percentages, 77 were grouped into this category with 37 grouped into the road sediment category and a further 109 were placed in the soil category. This may have been due to the fact that they were all sediment associated. For the soluble stormwater metal percentages, 190 were placed within this group with approximately 16% categorized within the deposit cannister category, indicating that the two groups were related, since they contained similar metal proportions.

The majority of the road sediment samples were placed within their own category (i.e. 61%), with a further 30% within the particulate stormwater category and 16.5% in the soil group. Once again indicating a relationship with each other which was probably sediment related.

The deposit cannister category had 74% placed within its own group with approximately 10% within the soluble stormwater group and 15% within the road sediment category. This indicated that on a some occasions the deposit cannister and road sediment samples had similar metal proportions, but for the majority of time the groups were quite distinct from one another. This could have been due to a specific source input to the catchment area during these periods.

Actual Group	Predicted Group Membership				
	1	2	3	4	5
1	77 (34.1%)	1 (0.4%)	37 (16.4%)	2 (0.9%)	109 (48.2%)
2	0	190 (84.1%)	0	36 (15.9%)	0
3	83 (30.1%)	2 (0.7%)	169 (61.2%)	4 (1.4%)	18 (16.5%)
4	1 (0.7%)	14 (9.9%)	21 (14.8%)	105 (73.9%)	1 (0.7%)
5	2 (4.8%)	0	4 (9.5%)	0	36 (85.7%)
Ungrouped cases (17)	3 (17.6%)	2 (11.8%)	9 (52.9%)	2 (11.8%)	1 (5.9%)

Table 13.3 Discriminant analysis predictive group classification.

Key: Group 1 particulate stormwater proportions
2 soluble stormwater proportions
3 road sediment proportions
4 deposit cannister proportions
5 soil proportions

The majority of soil values were grouped into their own category with small percentages occurring within the road sediment and particulate stormwater samples, once again indicating a similarity between the data sets.

The ungrouped cases were those of the unground road sediment samples and as would be expected were categorized within the road sediment category.

The Table therefore illustrates the overlap and similarity between some of the data sets. It took into account every single sample and therefore the results obtained were different from those given in Tables 13.1 and 13.2 where only the overall mean values were taken.

A stacked histogram (Figure 13.1) has been produced which gives a single plot of the cases. Since there was more than two functions a stacked histogram was produced based on the first two discriminant functions i.e. iron and lead. Each case is represented by a symbol of its group i.e. 1 to 5.

From consideration of the stacked histogram it can be seen that the majority of groups all occurred together, i.e. the same numbers were usually found together, indicating the set groups of the data. However, there were seen to be a few variations from this general pattern. For example, group 4 was located within group 2 at one end indicating a close relationship between the deposit cannister and soluble stormwater samples. Groups 1, 3 and 5 appeared to be somewhat mixed indicating similarities between the metal proportions within the particulate stormwater, road sediment and soil samples.

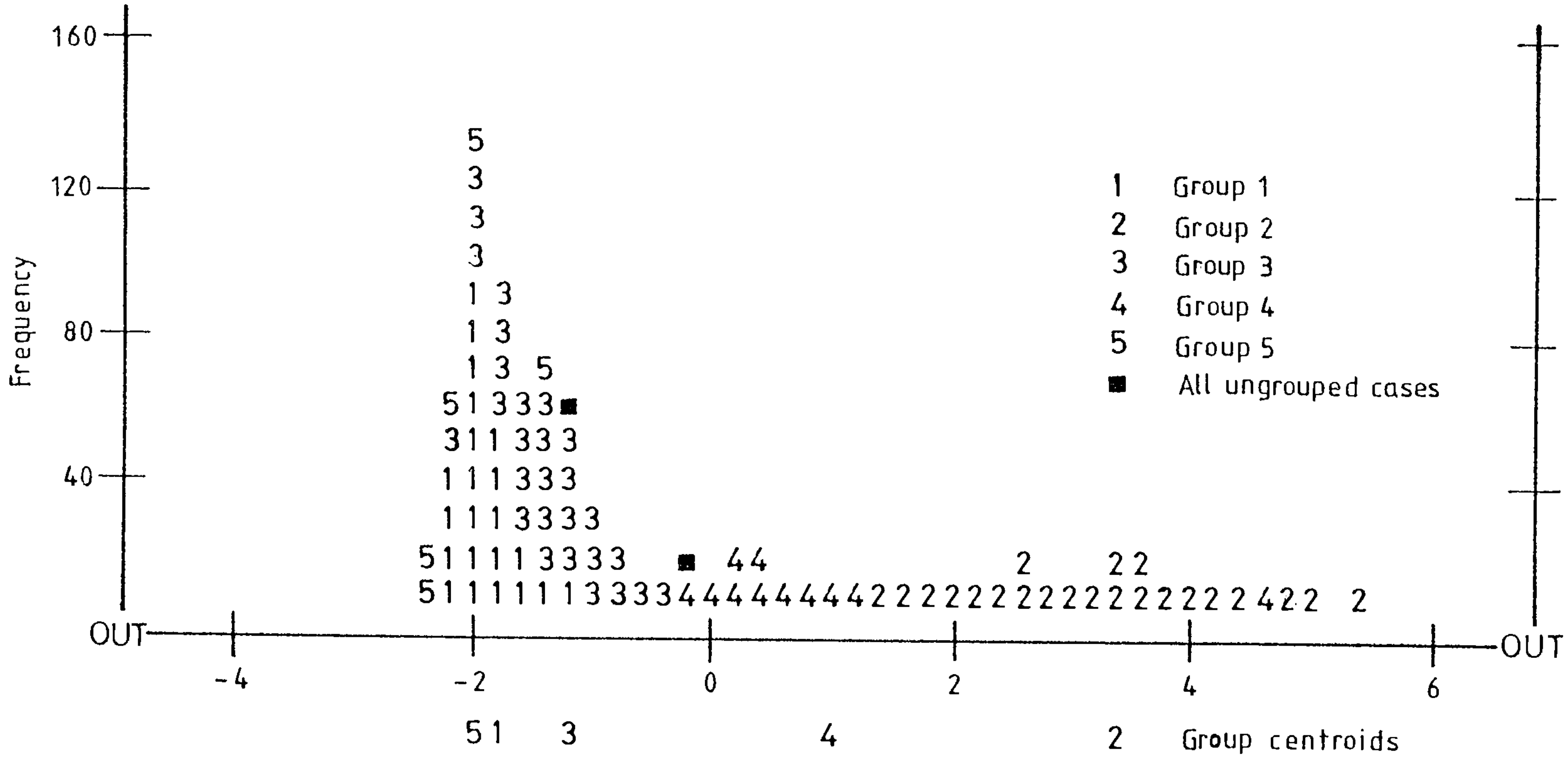


Figure 13.1 Discriminant analysis stacked histogram for all proportionate data.

The order of closeness between the groups was from 5 > 3 > 4 > 2. The soluble stormwater and deposit cannister groups tended to be more isolated and further from those of the soil, road sediment and the stormwater particulate samples, which tended to be more closely related to each other.

In conclusion, there appeared to be distinct groups within the proportionate metal data set. However, in some instances these were shown to overlap. The samples from the road sediments, soil and particulate stormwater samples tended to be more closely related then those from the deposit cannister and soluble stormwater samples. However, the latter two were sometimes observed to exhibit similar metal proportions.

CHAPTER 14

CONCEPTUAL MODEL FOR PATHWAYS UTILIZED BY HEAVY METALS IN URBAN STORMWATER RUNOFF

14.1 Introduction

From the study of extensive literature an hypothesis was forwarded for the various pathways utilized within the Chelmsley Wood catchment by the metal pollutants. The pathways are illustrated in Figure 14.1.

A programme of fieldwork was subsequently initiated in order to quantify the pathways. Over a 12 month period, from July 1983 to July 1984, aerial deposition rates were measured and road sediment and soil samples were collected. Rainfall and additional meteorological data were obtained from on site measurements and from local meteorological offices. Over the study period, stormwater samples were obtained from 19 separate events, 15 of which have been studied. All samples were analysed for the same heavy metals namely; iron, lead, zinc, copper, chromium, nickel and cadmium.

Information regarding road maintenance records (street sweeping and gully pot cleaning) and de-icing records were obtained from Solihull District Council. A traffic survey was also implemented with additional information obtained from the West Midlands Couny Council.

Due to the residential nature of the catchment area, metal inputs to the ground surface were assumed to be limited to normal suburban activities, aerial deposition, vehicular activity and anthropogenic sources.

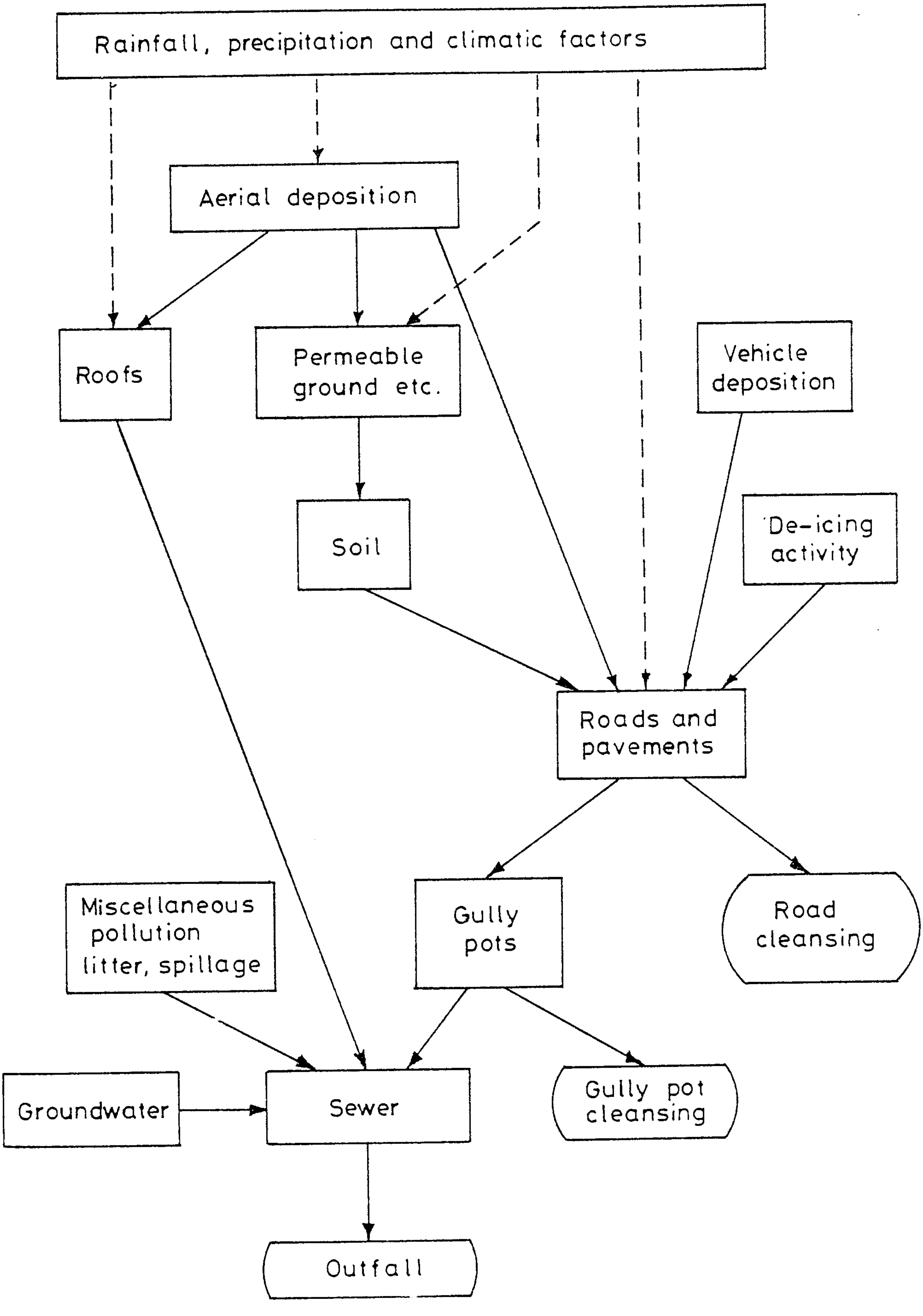


Figure 14.1 Pathways followed by metal contaminants during their passage through the catchment.

14.2 Inputs to the System

14.2.1 Rainfall and Precipitation

Rainfall and precipitation were measured by two tipping bucket raingauges located within the catchment area. Rainfall measurements were recorded onto a data logger and the tapes were later deciphered by Birmingham City Council. As there were only two raingauges within such a large catchment area, discrepencies often occurred between the recorded rainfall and the runoff, additional data was therefore obtained from a local meterological office.

14.2.2 Total Aerial Deposition

Aerial deposition, including rainfall and dustfall, were monitored monthly and were analysed for total heavy metals.

The aerial deposition falling onto roofs and paved surfaces was available for direct removal by surface water runoff, either in solution or in association with particulate matter. A proportion of the deposition products would fall onto permeable and semi-permeable ground and could also be washed directly into the sewer system with any surface runoff, but the majority would be carried into and enrich the soil metal store.

12.2.3 Soil

Through mechanisms of translocation and leaching metals would be removed from the topsoil and carried down through the soil profile at a very slow rate. Samples of topsoil and subsoil were taken at ten locations throughout the catchment (see Section 8.4).

Soil particles transported onto impermeable surfaces by erosion processes or by human activity could therefore be regarded as an input to the heavy metal load in the runoff. It would be possible for a small proportion of the metals within the soil store to enter the groundwater and be discharged directly into the sewer system as baseflow. Baseflow measurements were taken throughout the sampling period and the average metal concentrations within the flow were found to be negligible and were subsequently subtracted from the stormwater loadings.

Although it has been shown that soil forms a significant proportion of road sediment (Hopke et al (1980)), no relevant data were available for quantifying the input rate to the road surface. Road sediment samples were taken monthly during the sampling period at numerous locations throughout the catchment (see Section 8.3). The determinations of metal concentrations within the roads sediment samples, however, did not prove helpful in evaluating the rate of soil movement onto the road surface or in establishing direct metal inputs from traffic.

12.2.4 Road Surfaces

Additional inputs to the road surface other than that of soil movement onto roads, which is unknown at present, include direct deposition from vehicles, including vehicular breakdown products and de-icing products.

Vehicular activity within the catchment area was determined by a traffic survey. The survey revealed that the contribution from commercial vehicles was negligible whilst private vehicles predominated with motor vehicles providing a small presence.

Using information provided by the West Midlands County Council, the data collected were extrapolated to determine the vehicle kilometers travelled per day, during each week of the year. Mance (1981) stated that the prediction of pollution loadings, especially heavy metals, could be possible from the knowledge of the number of vehicle miles travelled along a given length of highway. It was also stated that the relationship could explain some of the difficulties in interpreting variations in stormwater quality from residential catchments, as traffic densities have seldom been reported.

However, evaluation of the metal input direct to the road surface and adjacent pavements and verges, which result from traffic flows encountered within the catchment, proved much more difficult to calculate. The literature showed that values of direct lead deposition per vehicle kilometer had been determined for various locations and conditions within the USA (Shaheen (1975), Christensen and Guinn (1979) and Ter Harr et al (1972)), but no comparable data were available for the UK (Garland (1985)). Little and Wiffen (1978) estimated that 9% of the lead emitted in vehicle emissions from motorway traffic was deposited within 100 m, but this was inappropriate for the short suburban driving cycle which was characteristic of the Chelmsley Wood catchment. Garland (1985) in consultation with Chamberlain suggested a deposition rate of 5 to 20% of the lead emitted would be appropriate. Therefore for the Chelmsley Wood site a deposition rate of between 9 to 20% of emitted mass would probably be anticipated.

A similar problem was encountered when attempting to assess zinc inputs. The majority of zinc input can be attributed to tyre wear (Hopke et al (1980)), but relevant data either relate to the USA (Christensen and Guinn (1979)) or were provided as a total tyre wear rate and the zinc content of tyres (Dannis (1974) and Cadle and Williams (1978)). As the zinc content of tyres varies widely depending upon the manufacturer, the best that could be obtained was a probable range of values for the deposition rate.

Although a number of studies have identified the products of vehicle exhaust emission, lubrication, wear and corrosion as sources of iron, copper, chromium, nickel and cadmium, none have been found to quantify the input rates to the road surface.

The records of de-icing activity obtained showed that on average 40 gm of salt were applied per square meter of road surface during each event, but only 40% of the total road area (i.e. priority routes only) were treated on each occasion. Since the source of road salt was the same as that discussed in the study undertaken by Hedley and Lockley (1975), the metal input resulting from this activity could be determined using the results of the analyses.

It was difficult to quantify unpredictable inputs resulting from anthropological activities such as roadside vehicle maintenance, fertilizer application to verge vegetation, refuse spillage and litter etc.. However, observations indicated that over the period of study such inputs were likely to be small, with the possible exception of vehicle maintenance activities.

14.2.5 Roofs

The only input to the roof itself was that of aerial deposition. This together with the products of roofing material breakdown, pass directly into the sewer system. The guttering was not metal and hence there was little additional metal input from the degradation of these products.

Although roofing materials and road surface degradation products contribute significantly to the inert solids in stormwater runoff (Ellis and Revitt (1982) and Harrop (1984)), within the study catchment, the direct input of metals from these sources were considered insignificant, with the possible exception of iron from the degradation of facing sand from roofing tiles.

14.3 Transport of Metals through the System

It was clear from the literature that the duration, volume and intensity of rainfall were prime factors in determining the quantity of material removed and transported by surface water runoff. Harrop (1984), using multivariate analysis found a strong correlation between washoff loadings and total surface runoff and event duration. In addition for lead and cadmium, flow and storm duration explained more than 90% of the observed variance and 79% of the variance in the zinc concentrations. Inspection of the data gathered in the research study suggested that storm duration, maximum rainfall intensity and flowrate were the most suitable parameters for use in the model when evaluating metal transport rates.

14.3.1 Roofs

Harrop (1984) deduced that roofs simply acted as a reservoir for pollutants deposited between runoff events. These pollutants are mobilized due to the steep gradients during the early stages of rainfall, either as deposited matter or in direct association with the inert breakdown products from roofing materials. It has been suggested that the process could provide a significant proportion of the first flush effect (Pratt and Adams (1984)). Roof runoff was not studied due to the large expanse of the catchment and the roofs discharged directly into the sewer system, therefore isolation of one in particular would have been very difficult.

14.3.2 Road Surfaces

The accumulation and removal of pollutants on road surfaces have been investigated by many research workers. Ellis (1979) and Ellis and Revitt (1982) in particular studied the distribution of heavy metals with the range of sediment particles found, in order to assess potential toxic effects and the effectiveness of street sweeping practices. Also discussed was the accumulation of sediments in surface depressions and against kerbings and the tendency of sediments to become sorted through the action of traffic and surface water runoff, all phenomena considered in the earlier studies of Sartor and Boyd (1972). Through their investigations Sartor and Boyd demonstrated that the rate at which rainfall washed loose particulate matter from the street surface was dependent upon rainfall intensity, street surface characteristics and particle size. It was shown that the washoff process could be simulated by the following equation:

$$N_c = N_o (1 - e^{-krt}) \qquad (14.1)$$

where: N_c is the weight of the material washed off the street,

N_o is the initial level of material on the street surface,

t is the time from the start of rainfall (mins),

r is the rainfall (mm/hr),

k is a constant dependent upon street surfacecharacteristics and ranges between 0.1 to 0.5 hr/mm.min.

Pollutants can therefore accumulate on road and pavement surfaces, and during rainfall be washed into the gully pot where they can either be retained, washed through or resuspended/reincorporated during high rainfall intensities and transported into the sewer system.

14.3.3 Gully Pots

The efficiency of roadside gully pots in removing the heavy particles entrained in stormwater runoff has been demonstrated in several studies (Pratt and Adams (1984), Mance and Harman (1978) and Fletcher et al (1978)). It has been estimated that for sediments less than 1 mm in size, those associated with heavy metals, the mass washed through the gully pot could exceed the mass retained by many times (Fletcher et al (1978)). In recent years, particular attention has been paid to the likelihood that the water stored in the gully pots may itself present a significant source of pollution and that prior to a rainfall event, the concentration of heavy metals tended to increase with time (Harrop (1984) and Mance and Harman (1978)).

The removal of liquors and sediments from gully pots have been investigated and simulated mathematically by Fletcher and Pratt (1981). It was found that a linear relationship existed between the rate of resuspension of bottom sediments and the incoming flowrate. For dissolved material, complete mixing occurred when the inflow rate exceeded 0.12 l/sec, below which there was a close correlation between the 'percentage of the gully pot mixed' and the inflow rate.

14.3.4 In-Pipe Deposition

Little information was available regarding the deposition in the pipes of separate stormwater sewer systems. Where the flow characteristics of the sewers are poor it has been suggested that solids settled during the recession limb of one storm hydrograph are re-entrained during the rising limb of the following one, thus contributing to the first flush effect (Ellis (1979)). Fortunately at Chelmsley Wood, visual inspection revealed the sewers to be self-cleansing.

14.4 Losses from the System

All inputs deposited on impermeable surfaces are available for removal by stormwater runoff, except that which is removed by street cleaning processes. However, the fraction of aerial deposition falling on permeable and semi-permeable surfaces that can be removed in this way are probably small and the majority will enter the soil store. Indirectly some may find their way back into the system through groundwater or when the soil particles are transported onto impermeable surfaces.

14.4.1 Road Maintenance Practices

Street sweeping and gully pot cleaning records were obtained for the entire sampling period. The efficiency of street sweeping practices have been the subject of several research projects and recently work in the USA has been summarized by Sartor and Gaboury (1984). Sartor and Boyd (1972) found that 50% of the metal loading in roadside dust were associated with particles smaller than 0.043 mm. Ellis (1979) concluded that 30% of heavy metals were associated with material below 0.06 mm in size and that between 40 and 90% of all pollutants were found within particulate matter less than 0.2 mm in size.

All street sweeping studies have shown that the removal efficiency increases with increasing particle size. For mechanical rotating sweepers in the UK, nearly 100% removal is achieved for particles greater then 10 mm, this falls to 50% for the range of particle sizes between 1 and 10 mm, but for the fraction below 0.06 mm only 15 to 20% removal is likely (Ellis (1979)). Given the particle size range with which the majority of metals are associated, it is unlikely that as much as 20% is removed during each event.

Gully pot cleaning was infrequent and not complete for the catchment area, therefore the loss via this pathway was assumed minimal, an assumption that could be grossly inaccurate.

Apart from the two main losses from the system, that of removal in road maintenance practices and the discharge into the soil sink and groundwater, an additional loss may be encountered by the atmospheric loss by wind. This however, would be extremely difficult to determine, if not impossible.

14.5 Discharge to the Receiving Watercourse

At the study site, once the stormwater sewer left the catchment, it passed under both the feeder road and the M6 motorway where it discharged into an open channel, which subsequently discharged into the River Cole.

A limited study undertaken in 1984 to 1985 (Payne (1985)) revealed that in general, the metal content of sediments taken from the bed of the channel into which the stormwater discharged, were higher than in the soils from the surrounding sides and adjacent fields. The levels of metals within the drain sediments were often up to seven times greater than those found within the subsoil close to the outfall. In particular, banks of sediment were found where the metal content was significantly higher than that at other locations. With the exception of a shoal at the sewer exit, these banks were observed to migrate gradually downstream towards the River Cole. The proportions of metals found within the drain sediments, although similar to those found in the soil, were more closely related to those found within the stormwater runoff. It was therefore concluded that the contamination of the drain sediments was a direct result of the stormwater discharge. Further work will be needed if the actual levels discharged and accumulated within the stream bed sediments are to be assessed with any accuracy.

14.6 The Model

A flow diagram illustrating the essential components of the model, describing heavy metal movement through the Chelmsley Wood catchment is presented in Figure 14.2.

Figure 14.2 Flow diagram illustrating the essential components of the model decribing heavy metal movement through the Chelmsley Wood catchment.
(Hedges et al (1985))

Figure 14.2 continued Flow diagram

Figure 14.2 continued Flow diagram

14.6.1 Principles behind the Model

The following storage equation represents the foundation on which the model was built:

$$I - O = \Delta S \qquad (14.2)$$

where: I is the input to the system,

O is the output from the system,

ΔS is the change in storage within the system.

Inputs to the system entered one of three stores: roof, road and pavement, and permeable and semi-permeable land, and the metals were allowed to accumulate within these until a storm event occurred. Inputs based on observed aerial deposition rates, traffic flows and soil movement rates were added to the relevent stores on a daily basis. Relationships have been derived from road dust analyses which provided a crude measure of the rate of soil input to road surfaces as a function of traffic activity, the preliminary analysis, given in Appendix B, and the relationship for lead is shown in Figure 14.3.

The rate at which material left a particular store once a storm event occurred was governed by a "removal time". Each store represented a particular class of land cover and the removal time was taken to be the rainfall duration required to wash all accumulated material from that surface. Thus, if the accumulated metal within a particular land class was M gms, and the removal time was taken to be Tr minutes then throughout a storm M/Tr gms were removed each minute until the store was exhausted. Consequently, if the storm duration was less than Tr minutes, only a portion of the store would have been removed, conversely if the duration was greater than Tr minutes, it would be emptied.

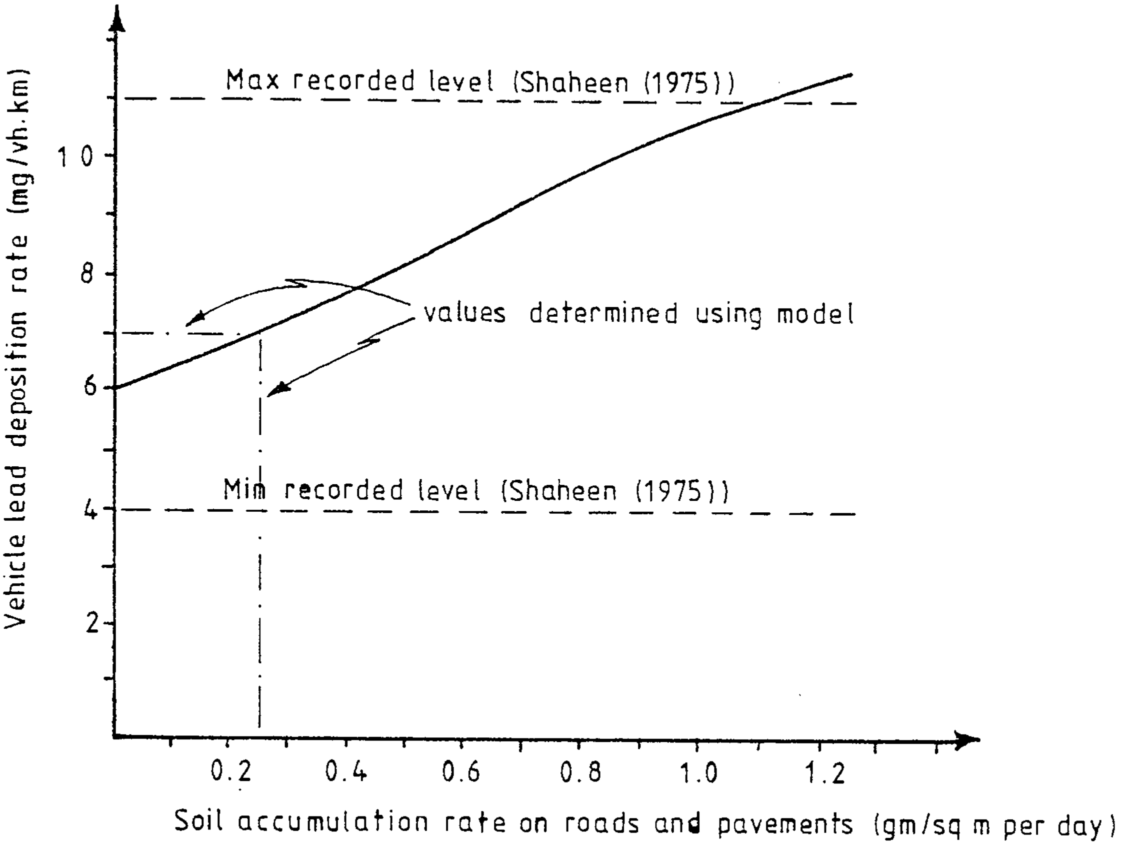


Figure 14.3 Relationship between vehicle lead deposition rate and soil accumulation rate derived from analysis of road dust.

Since the sewer was self-cleansing, it was assumed that once material was mobilized it would be transported through the entire length. The transport through the sewer was simulated using the travel time in the same way that the removal time was employed for land surfaces. However, an option has been retained for the use if the sewer was not self-cleansing. In this instance material being routed through the sewer is deposited in a sewer store as soon as the storm ends, and is re-entained during the next event.

The pathways taken by metal contaminants during their passage through the catchment are assumed to be as illustrated in Figure 14.1. Each input enters, on a daily basis, and accumulates in an appropriate store as described above. Data were arranged in such a way that when street sweeping or de-icing activities took place, material was either removed from, or added to, the road and pavement store on that day. The washoff process was simulated by transferring material from one store to the next until it entered the sewer and was discharged from the system. The transport process was modelled in minute steps throughout the duration of each storm event. Thus metal accumulated on roofs was washed directly into the sewer, but the fraction of aerial deposition directly available for removal from permeable and semi-permeable areas would pass through the road and pavement store before entering the sewer. If two or more storms occurred on the same day, only the material remaining in the store at the end of the first event was available for removal during later storm events.

The catchment was divided into a number of zones each representing areas of differing distances from the sewer outfall. Material entering the sewer from the zone furthest from the outfall had to travel through each subsequent section of sewer before leaving the system.

14.6.2 Refinements

When a modified form of Sartor and Boyds equation (equation 14.2) for simulating washoff from street surfaces was applied instead of the "removal time" concept, simulation accuracy improved. If the exponents r and t in equation 14.2 are regarded as cumulative rainfall R, then the quantity of material removed during one minute interval at time t minutes (N_t) is given by:

$$N_t = S_u - S_o e^{-kr} \qquad (14.3)$$

where: S_u is the material remaining in store at the end of the previous minute interval,

S_o is the material in store at the start of the storm.

Material entering the road and pavement store from the permeable and semi-permeable land store had already been mobilized and thus followed the transport process previously described using an appropriate removal time.

It was noted that storms producing a low total rainfall tended to give high total metal discharge values when compared with observed levels, and that the values obtained for those with a high maximum rainfall intensity were too low. One obvious explanation was that the model possessed no facility for simulating the roadside gully pots. A new store was therefore introduced between the road and pavement and sewer stores.

Finally it was reasonable to assume that at high rainfall intensities, the effects of raindrop impact and high runoff velocities would result in additional soil movement. In the model it was simply assumed that there was an additional input of soil to the paved areas if the maximum rainfall intensity exceeded a given value.

14.6.3 Proving the Model

Data from sixteen storm events were used to calibrate the model, a process which highlighted significant deficiencies in the available information.

The first problem encountered was the determination of a suitable value for metal deposition direct to the road surface as a result of vehicle activity. Briefly this consisted of an iterative computer process from assuming a given soil input rate, by trial and error the metal input to the road surface by vehicles was calculated. This was then correlated to the metals in the road sediment that were measured (see Appendix B).

Although relationships of the form described in Figure 14.3 had been developed for most metals under consideration, no specific deposition rate could be identified for any one of the metals concerned. Had just one been found, this would have fixed the soil input rate to the road surface, which in turn would have enabled deposition rates for each of the remaining metals to be obtained. A literature search had revealed that lead input rate to the road surface provided the smallest range of possible values (4 to 11 mg/vehicle kilometer) and as a consequence all proving work was concentrated on lead. A value of 7 mg of lead per vehicle kilometer (veh km) travelled, yielded the best results, and from Figure 14.3 it was indicated that the average daily rate of soil accretion on the road and pavement surfaces was 0.25 mg/sq m. Thus using similar relationships to Figure 14.3 for some of the other metals, the immediate deposition rates due to vehicle activity were obtained and these are shown in Table 14.1. It was recognized that these values, especially that for lead, would vary in response to climatic and other factors, but no relevent information was available and hence no allowance for such changes could be incorporated in the model.

When the rainfall/runoff data were examined for the storms used to prove the model, no simple relationship between duration of rainfall and runoff hydrograph duration could be found. Two patterns were revealed, either rainfall duration exceeded that of runoff or the reverse (Figure12.21). As Harrop (1984) had found storm duration to be a better parameter than rainfall duration for correlation with total metals discharged, runoff duration was substituted in the model as the time during which metal removal took place.

Metal	Deposition Rate mg/sq m per day
Lead	7.0
Zinc	2.0
Copper	0.6
Chromium	0.3
Nickel	0.2
(Soil accumulation rate = 0.25 gm/sq m per day)	

Table 14.1 Metal inputs direct to road and pavement surfaces as a result of vehicle activity.

Other parameters used in the model were initially obtained wherever possible, through a judicious selection of values from the literature. Where data were not available or selected values proved inappropriate, adjustments were made through a process of trial and error until the best agreement possible between the observed and modelled total lead discharges were achieved.

14.6.4 Results

At the current stage of development the fixed parameters used in the model are as shown in Table 14.2, all of which could be varied at the operators discretion.

Observed and simulated values for total iron, lead, zinc, copper, chromium and nickel discharged, during each of the storms used in calibrating the model, are given in Table 14.3. A simple statistical analysis indicated that the agreement between model and actual outputs was better than would appear at first sight.

Lead and zinc provided the best simulations with excellent correlation coefficients of 0.989 and 0.974 respectively. Copper simulations were also good but had a lower correlation coefficient. Chromium simulations were fairly good but not as good as lead. This could have been due to a number of factors including, analytical errors during the sampling program, for on a number of occasions chromium depostion rates were zero, the vehicle input rate could also be in error as with the Sartor and Boyd equation.

Total catchment area	107 ha
Proportion of area - roofs	22 %
Proportion of area - roads and pavements	15 %
Removal/Travel times	
Roofs	4 min
Roads and pavements	10 min
Permeable and semi-permeable land	40 min
Sewers	23 min
Number of zones	4
k	0.1 hr/mm.min
Vehicle depostion rate	(as per Table 14.1)
Proportion of material removed each street cleaning event	20 %
Accumulation of soil on roads etc.	0.25 gm/sq m per day
Aerial deposition lost to permeable and semi-permeable land	90 %
Proportion of metal in soil %	(as per analysis)
Input from breakdown of roofing materials	0.00 mg/sq m per day
De-icing activity	
Weight of salt input per event	40 gm/sq m
Proportion of metal in salt	(as given by Hedley and Lockley (1975))
Proportion of roads salted per event	40 %
Additional soil movement for high intensity rainfall	0.50 gm/sq m
Rainfall total above which gully pot trapping is ineffective	1.80 mm
Minimum rainfall intensity for removal of material trapped in gully pots	25 mm/hr

Table 14.2 Parameters input to program for simulation of heavy metal output from Chelmsley Wood.

DATE	TOTAL METALS gms											
	LEAD		ZINC		COPPER		CHROMIUM		NICKEL		IRON	
	Obs	Mod	Obs	Mod	Obs	Mod	Obs	Mod	Obs	Mod	Obs	Mod
16/08/83	265	205	368	152	83	76	39.9	8.3	23.6	8.2	3677	2436
16/09/83	164	186	150	311	38	90	11.7	34.9	39.6	16.7	2723	12480
10/10/83	28	43	51	42	8	11	4.0	0.9	20.6	0.5	1481	403
10/10/83	294	229	200	107	68	31	19.2	10.0	52.7	6.1	2266	1363
02/11/83	399	284	15	267	81	74	44.0	32.0	247.3	17.3	8575	8561
03/11/83	81	156	2	214	30	43	30.9	17.8	249.1	14.6	1036	1094
03/11/83	1.2	0.1	0	0	0.4	0	0.2	0.005	1.6	0.003	7.4	0.6
25/11/83	552	885	380	491	574	161	273.3	47.1	283.4	57.1	5051	5881
17/12/83	18	40	4	29	3	8	0.8	3.2	3.4	6.4	93	300
17/12/83	174	29	68	12	19	3	10.2	1.8	41.4	1.5	1426	269
02/01/84	222	217	151	96	39	28	11.9	13.3	28.8	13.7	1074	1580
24/05/84	3216	3016	2382	2274	511	676	154.2	277.9	338.2	184.9	35149	69618
25/05/84	49	147	95	86	22	30	6.3	9.5	10.6	12.2	539	2287
20/06/84	61	76	63	30	18	10	12.8	3.9	58.6	4.0	922	5272
20/06/84	343	406	347	159	70	52	38.2	20.9	146.0	21.3	5339	3038
15/07/84	47	11	39	5	6	2	2.7	0.6	15.0	0.6	6037	72
Mean	397	371	270	267	98	81	41.3	30.1	97.5	22.8	4712	6872
Std dev	775	737	578	552	176	164	72.2	67.5	115.1	45.4	8477	17090
Corr co	0.989		0.974		0.774		0.544		0.717		0.966	

Table 14.3 Comparison of heavy metal discharge for observed and modelled events.

Key: Obs - observed
Mod - modelled
Std dev - standard deviation
Corr co - correlation coefficient

The correlation coefficient for iron was excellent (0.96) but the mean and standard deviations were far too high, indicating a constant error. This could have been due to the wrong travel time used, as iron may have been bound to larger particles having slower transport rates than that used in the model. Also, no allowance was made for vehicular input as it was considered negligible compared with that from soil and aerial deposition. Additional sources and sinks were not considered, such as gully pot cleaning (since no data were available at the time of the model development) and no roof input was included.

With nickel the correlation coefficient was quite good, but the mean and standard deviations were consistently low, again indicating again a constant error. This may have been due to the reasons given for chromium and iron i.e. error in sampling, zero nickel deposition in some cases, wrong value of k used in the Sartor and Boyd equation, errors in vehicle deposition rate and incorrect travel times used as the data input to the model assumed that nickel (and all other metals) were bound to the same particle sizes as lead which may not necessarily have been the case.

Cadmium was rejected from the modelling analysis due to the road dust analysis program experiencing extreme sensitivity to changes in cadmium concentration. No consistent values could be obtained, therefore the program was not run for cadmium.

Iron, nickel and cadmium were therefore rejected from further analysis at this stage since there was an indication of consistent errors that which could not be adequately explained. Lead, zinc and copper provided the best analysis with chromium proving to be fairly good.

Since the sample was relatively small, further checks were carried out by comparing average metal concentrations (total load discharged divided by total flow) and average output rate (total load discharged divided by hydrograph duration) for actual and modelled events, both of which yielded adequate results (Hedges et al (1985)).

If simulation of sixteen proving storms is considered satisfactory then a measure of the total inputs to, and outputs from, the catchment for the twelve months of the study period could be obtained from the model. A summary of the results for lead, zinc, copper and chromium are given in Table 14.4.

As no information was available on the gully pot cleaning at the time of model development, the positive storages at the end of the year may not be correct and may therefore, to a small extent invalidate the results. Lack of gully pot cleaning would partly account for the positive stores, which would subsequently be removed during gully pot cleaning events.

Furthermore, the model provided outputs for each individual rainfall event which would have caused the initiation of the stormwater sampler. The values could be used to study either the impact of individual events or the seasonal variations in the pollution loadings experienced by the receiving watercourse. Figure 14.4 have been drawn to display the monthly variations in the mass lead, zinc, copper and chromium discharged from the Chelmsley Wood catchment together with that of total monthly rainfall.

	LEAD (gms)	ZINC (gms)	COPPER (gms)	CHROMIUM (gms)
INPUTS				
Aerial deposition	39255	47674	12768	2236
Vehicle input	44137	12421	3657	1671
Soil input to roads	3203	10686	3055	1540
De-icing input	559	385	0	302
OUTPUTS				
Dicharged in runoff	48718	36020	11189	4006
Lost in soil store	22257	27031	6434	1268
Removed in sweeping	8219	3778	1085	472
MASS BALANCE				
Total inputs	87154	71166	19480	5749
Total outputs	79194	66829	18708	5746
Change in storage	+ 7960	+ 4337	+ 772	+ 3

Table 14.4 Summary of metal inputs to, and outputs from, the Chelmsley Wood catchment between 20/07/83 and 18/07/84.

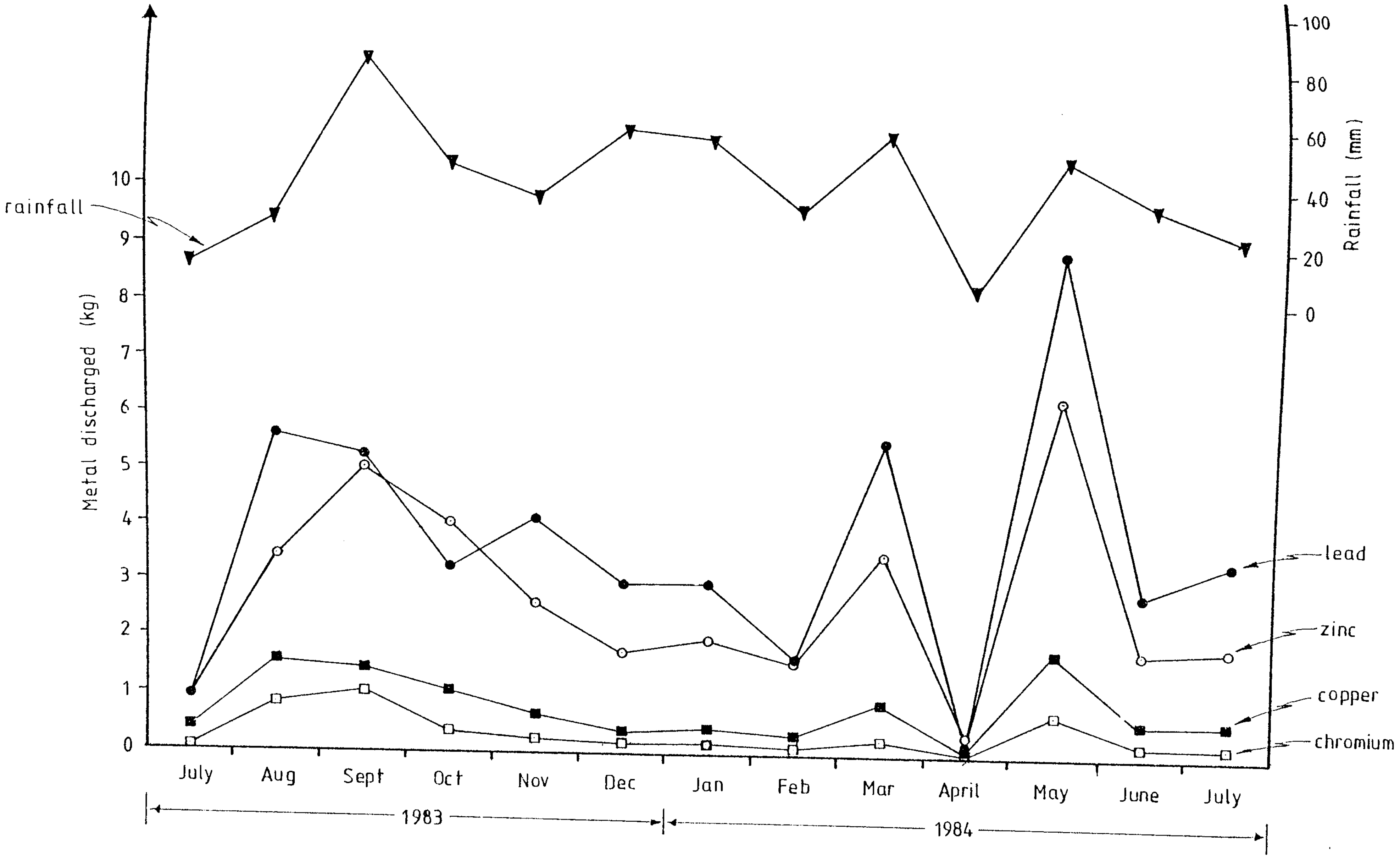


Figure 14.4 Mass of metals discharged in surface runoff per month and total monthly rainfall.

The monthly plots of the heavy metals discharged within the runoff showed marked seasonal variations. The minimum loading of all metals considered were found in April, followed by a high peak metal runoff during May. This was probably attributable to the very low total rainfall during April (see Figure 14.4), allowing a build up of contaminants, which were subsequently removed in the runoff during heavy rainfalls in May.

In order that comparisons could be made between the heavy metal deposition (Chapter 9) and that of the stormwater runoff loads, the metal loads within the stormwater runoff were calculated for the duration of the deposition sampling periods. The total rainfall together with the total vehicular deposition for these periods was also calculated. The values are given in Table 14.5.

Both the metal stormwater runoff loads and metal deposition rates exhibited seasonal variations but were not consistent in all cases. However, one noticeable correlation was observed and this was between the low runoff loads of lead to that in deposition and in vehicle deposition during April. This was also seen to be well correlated with low total rainfall during this period.

Since few correlations could be seen from the visual inspection of the data, a correlation matrix was performed on the data. Excellent correlations were found between each metal within the runoff loads for both the monthly figures, and between deposition sampling periods. Additional fair correlations were also found between the total monthly rainfall and the monthly zinc runoff, with a correlation coefficient of 0.66.

Month	Total R/F (mm)	Stormwater Runoff (kg)				Vehicle Deposition (kg)			
		Pb	Zn	Cu	Cr	Pb	Zn	Cu	Cr
1	19.8	2.19	2.34	0.90	0.16	1.81	0.52	0.15	0.08
2	58.0	8.25	5.69	2.18	1.00	3.13	0.89	0.27	0.13
3	66.2	3.03	2.67	0.71	0.17	4.47	1.28	0.38	0.19
4	32.2	2.46	3.52	0.94	0.94	2.80	0.80	0.24	0.12
5	20.9	3.76	2.18	0.58	0.19	1.93	0.55	0.16	0.08
6	76.0	3.94	1.96	0.53	0.25	4.50	1.28	0.38	0.19
7	29.6	2.13	1.62	0.36	0.17	3.92	1.12	0.33	0.17
8	26.6	1.78	1.64	0.36	0.13	4.45	1.27	0.38	0.19
9	47.4	5.58	3.55	0.89	0.30	2.80	0.80	0.24	0.12
10	1.0	0.25	0.39	0.09	0.03	0.85	0.24	0.07	0.04
11	28.6	5.60	4.18	1.15	0.47	1.67	0.48	0.14	0.07
12	47.2	5.77	4.18	1.23	0.49	3.81	1.09	0.33	0.16
13	25.6	3.90	2.08	0.67	0.25	1.76	0.50	0.15	0.07

Table 14.5 Total rainfall, stormwater runoff metal loads and total vehicle deposition between deposition sampling periods.

The total rainfall between sampling periods was fairly well correlated with all of the metals deposited from vehicles, with correlation coefficients ranging from 0.6 to 0.8.

14.6.5 Discussion

The original purpose of the model was to evaluate the hypotheses developed as a result of site investigations, undertaken in order to study the pathways taken by heavy metals as they travelled through the catchment. In practice the construction of the model proved more demanding than was originally envisaged and revealed shortcomings in the data available for its calibration.

The model dealt with the soluble and solid phases of metal transport together and it was believed that a better simulation of events would be achieved if the phases were catered for separately, but in parallel, within the program. This would necessitate the addition of functions to allow the leaching of metals associated with sediments. At the time of model development such modifications were not feasible due to the very limited size of computer memory available (BBC Micro 40K).

Only after a lengthy process of trial and error was calibration of the model possible. This process was necessary due partially to the simple approach adopted, but in the main as a result of limitations within the data available. Difficulty relating to the determination of inputs from vehicle activity and the uncertainty simulating the effects of gully pots were experienced.

Another area which needs further investigation is the question of inputs resulting from the breakdown of roofing materials. Although model simulations for lead, zinc and copper indicated, as suggested in the literature, contributions from this source were insignificant, if not zero, the lack of information deterred any attempt to simulate the transport of iron through the catchment.

Sartor and Boyd proposed a relationship for the simulation of washoff processes from road surfaces in 1972. Jewell and Adrian (1981) have noted that since its publication many researchers have utilized equation 14.1 in models, apparently without questioning its validity. In determining the best estimate for k, the constant in equation 14.1, it was found that a value of 0.1 produced the best overall results. However, when alternative values were used the agreement between observed and simulated outputs improved for some storms, whilst for others it deteriorated. Figure 14.5 indicates that for events 1 to 5 the results were generally better using $k = 0.2$ rather than 0.1 and the reverse for events 8 to 15. Although not investigated in any great detail, it is also suspected that there may be different optimum values of k for each metal. Questions were therefore raised regarding the constancy of k in equation 14.1. There may be a temporal variation and its value could be independent of sediment particle size as suggested by Sartor and Boyd (1972).

Although the model allowed for temporal variation in most of the input variables, no attempt was made to simulate spacial variation. Mean values of aerial deposition, vehicle activity and metal content of soil have been taken as representative of the whole catchment, whereas in practice, spatial variation in all of these parameters have been observed.

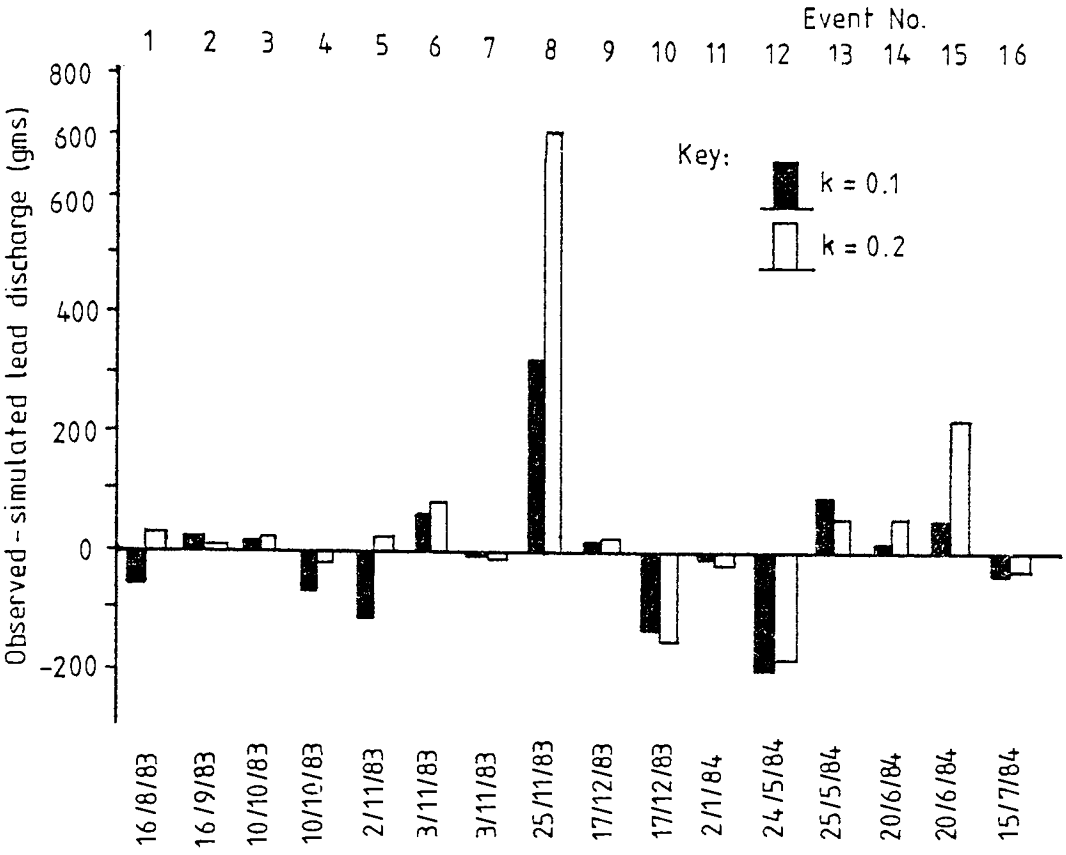


Figure 14.5 Effect of varying k on the difference between observed and simulated discharges of lead.

Housing and gully pot density were assumed to be uniform as was the distribution of the area covered by roads and pavements. All these factors, when combined with the effects of depression storage, localized accumulations and unpredictable incidents (e.g. garbage and oil spillage) render accurate simulation of events very difficult.

The results achieved for lead, zinc, copper and chromium, using the Chelmsley Wood model were considered reasonable. Testing of the model was incomplete and even when complete the model would be of little general value if it was specific to Chelmsley Wood and could not be used to predict outputs from other small catchments.

Finally there is the potential for developing the model itself. The basic processes are all present, albeit in a rudimentary form, and it will be possible to improve simulations by substituting more accurate functions to represent these processes. Currently pollutographs cannot be modelled, but this should be possible following the addition of a facility for inputting observed rainfall patterns, where such data is available.

14.6.6 Conclusion

The Chelmsley Wood model though simple in design has been shown to simulate observed events with a reasonable degree of accuracy. Furthermore, it has been used to obtain mass balances for lead, zinc, copper and chromium over a twelve month period of site investigations and to produce monthly (seasonal) variation in the metals discharged to the receiving watercourse.

Proving the model revealed serious shortcomings in the data available for its calibration and further detailed research is required to evaluate the following:

(i) the rates of accumulation of metals on road surfaces as a direct result of vehicle activity,

(ii) the rate of soil movement onto road and pavement surfaces,

(iii) metal inputs to the system resulting from the breakdown of roofing materials,

(iv) the accumulation of material in gully pots and surface depressions and their re-incorporation in runoff,

and (v) the acceptability of Sartor and Boyds washoff equation for simulating pollutant removal from road surfaces, especially the constant k in equation 14.1.

Calibration of the model, when combined with relationships derived using data gathered on site, suggested that metal input rates, direct to the road surface, from the urban driving cycle characteristic of Chelmsley Wood, were as given in Table 14.1. It was also estimated that the average rate of soil accumulation on road and pavement surfaces was 0.25 gm/sq m per day.

In conclusion therefore, the outcome of the model indicated that the hypotheses developed concerning the pollution pathways were essentially correct, as reasonable agreement was found between the observed and simulated events. The mean, standard deviations and correlation coefficients were also within acceptable limits. However, further information is required on roofs, gully pots and the Sartor and Boyd equation.

Cadmium was not included in the model as it was rejected within the road dust analysis section (Appendix B). Iron was also rejected as it was thought to be coming from roof degradation materials and this could not be modelled.

The model could also provide the foundation for the development of a general conceptual model for simulating the movement of heavy metals and other pollutants through small catchments. Such a model would provide planners and designers with a useful predictive tool.

CHAPTER 15

CONCLUSIONS

15.1 Introduction

From the extensive literature search an hypothesis was developed for the various pathways utilized by metal pollutants within a given catchment area. A programme of fieldwork was initiated in order to quantify the pathways. Samples of atmospheric deposits, road sediment, soil and stormwater were taken over a twelve month sampling period. A simple conceptual computer model was later designed (Hedges et al (1985)), in order to study and evaluate the pathways taken by the heavy metals as they travelled through the catchment.

The main objective of the study was to obtain the maximum amount of detailed water quality data possible for a limited number of storms, rather than a superficial study of many storm events.

Much time was required in the installation and calibration of the various equipment, collection and analysis of samples, and the analysis of data. The findings reported here are derived from the analysis of a limited number of storms. It would be necessary to analyse data from many more storms before any definite conclusions can be drawn and to allow a confident prediction of the storm pollution loadings.

15.1.1 Problems

Several practical problems were encountered during the establishment of the monitoring system. Both the Arkon flow recorder and the automatic sampler had previously been installed. When the Phox system was included difficulties were encounterd in balancing the division of flow between the Phox system and the sampler. In addition a larger peristaltic pump had to be purchased, to enable adequate flows to be achieved.

The sequence of the monitoring cells in the Phox system was discovered to affect the readings of the other probes. Laboratory tests before installation in the field revealed that the best sequence for least interference was the turbidity cell first, followed by the dissolved oxygen, conductivity, chloride, pH and temperature probes. Once installed little difficulty was experienced in the regular calibration of the system. The Phox system also required a flushing system to be installed. This was to ensure that the tubing, cells and probes could be cleaned after each event and a relatively sterile environment maintained whilst the probes themselves were kept wet.

When the sampler inlet tube was left free in order to prevent debris accumulating behind it, it had a tendency to be swept out of the flow. At such times, no samples were obtained. The tube was later fixed in the line of the flow to prevent this from occurring.

The Arkon flow monitoring device was adequate for the study but a few problems were encountered, and it is thought that a new flow monitoring device would be required for future studies.

The most frustrating problem was that of vandalism. Originally 24 deposit cannisters were set out on a regular grid pattern. In spite of being fixed on lampposts more than 5 m above ground level, vandalism forced the network to be reduced to 11 rather random locations, which proved to be the least likely attacked. One of the raingauges on the first floor of a school was also seriously damaged by vandals, and was out of action for some time.

The raingauges did not give representative results for the entire catchment area and often large discrepencies were observed between the recorded rainfall and runoff. This was the reason why the rainfall characteristics were not included on the storm hydrographs/pollutographs. It is thought that a greater number of raingauges stationed throughout the catchment would give better results.

The major conclusions drawn from each of the Sections of the research programme will now be discussed on an individual basis.

15.2 Deposition

From the deposit cannister study it was concluded that the area of Chelmsley Wood under study was not subject to significant levels of heavy metal deposition when compared with those from industrial areas, and the average metal deposition rates found within Chelmsley Wood during the study were within the ranges reported for other rural/urban areas.

Some of the metals showed seasonal variations in the deposition rates, the most prominant being iron, which was found to be greater during the summer months.

Slight spatial variation was also observed within the metal deposition rates and there was some indication of metals, especially lead, declining with distance from the motorway.

In order to study in more detail the the various influencing factors on metal deposition, it would be necessary to install a greater number of deposit cannisters on a more regular basis than used in the study.

15.3 Road Sediments

The heavy metal concentrations observed within the road sediment samples taken within the area were seen to be comparable with contemporary studies from other urban/residential areas.

Zinc concentration was often found to be elevated, the probable source for this may have been vehicles or from local agriculture. High concentrations of zinc were also found within the soil samples.

With the exception of lead, no distinct seasonal pattern could be identified within the road sediment metal concentrations.

Spatial variation was observed for the road sediment metal concentrations, with metal concentrations highest adjacent to the main entry points to the catchment and in close proximity to the feeder road/motorway and were lowest within the secluded/quiet residential areas.

15.4 Soil

The metal concentrations within the soil samples appeared to be similar to other related studies for urban/residential soils. However, one location experienced extremely high metal concentrations, which could have been due to some local contamination within the catchment area or from contamination outside the area before importation of the soil into the area.

Soil samples taken adjacent to major roads tended to exhibit elevated metal concentrations, suggesting that motor vehicles could be a likely soure of contamination.

15.5 Stormwater Runoff

15.5.1 Storm Hydrographs

Heavy metal concentrations were found to vary significantly throughout runoff events and from storm to storm. The relationship between water quality and rate of flow was unique for each storm. In some cases a 'first flush' effect was observed and a number of storms showed secondary and multiple peaks within the metal concentrations.

The peak metal concentrations did not occur simultaneously which may have been due to their different origins and ease of mobilization. The soluble metal concentrations often showed a similar trend to that of the particulate metals.

Cadmium was often found to be loaded onto the storm hydrograph at a later time. This has also been observed by Ellis (1982) who suggested that it was due to the fact that cadmium was associated with a different source and contributing area and only becomes loaded onto the hydrograph when that particular area of the catchment becomes effective.

15.5.2 Correlations

Correlation matrices for individual storm events were shown to vary considerably from one storm to another and between the metal phases. However, in many cases metal concentrations appeared to be well correlated to one another as was the case for the road sediment, deposit cannister and soil samples. Negative correlations were found between the metal concentrations and the time from the start of the storm.

15.5.3 Average Stormwater Metal Concentrations

The average stormwater metal concentrations were calculated as flow weighted mean concentrations. These, however, did not provide an adequate description of the runoff hydrograph since wide variations existed, but they did allow data from different sources to be compared. A consistent flow weighted mean concentration for each pollutant was not found for the catchment.

15.5.4 Total Storm Loads

The total storm loads were calculated in order to assess the quantity of metal pollutants discharged during each runoff event. The metal loadings were found to vary considerably from one storm to another, and were probably a result of a number of interacting variables.

The total storm loadings appeared to be well correlated with the flow weighted mean concentrations. The total storm loadings were shown to be strongly correlated with the total flow (volume), with the current rainfall characteristics (especially the maximum rainfall intensity), and to a lesser extent on the rainfall characteristics of events prior to the runoff event.

The maximum concentration was found to be correlated to the flow weighted mean concentration.

The hydrologic parameters were also seen to be strongly correlated to each other e.g. between total rainfall and total flow, with a correlation coefficient of 0.86, and between total rainfall and duration of the storm, with a correlation coefficient of 0.96.

15.5.5 First Flush

Plots were made to estimate the mass of the first flush as described by Tucker (1975). However, only in a couple of events was a calculation feasible so the mass of the first flush was only calculated where it was possible to do so.

15.5.6 Cumulative Metal Percentages

The percentage of each metal discharged during each time step was calculated, however, only the results pertaining to the total metals were discussed. Generally, higher percentages of the soluble metals were discharged earlier than their particulate counterparts. In many storms approximately 50% of the metals were discharged during the first half of the storm duration, whilst in others, 50% of the metals were discharged within one third of the storm duration.

During a couple of the storm events a large proportion of the metals were discharged within a very short period of time.

This was a very interesting topic of study and it could become very useful for design purposes. If the time in which the majority of pollutants are discharged is known then treatment facilities could be installed in order to reduce the pollutant load by treating the most contaminated portion of the runoff. Further research is therefore needed in this particular aspect of study and it would also be interesting to look more closely at the individual metals discharged since only the total metals were studied here.

15.5.7 Soluble : Particulate Metal Ratios

The soluble:particulate metal ratios were found to display considerable variation with time throughout a specific storm and between storm events. Once again only total metals were discussed and it is thought that the individual metals would display different patterns and could form a topic of further research.

15.6 The Model

The Chelmsley Wood model though simple in design was shown to simulate observed events with a reasonable degree of accuracy. It has also been used to obtain mass balances for lead, zinc, copper and chromium over the twelve month period of site investigations and produced monthly variations for these metals discharged to the receiving watercourse.

Proving the model, however, revealed serious shortcomings in the data available for its calibration and further detailed research is required to evaluate:

(i) the rates of accumulation of metals on road surfaces as a direct result of vehicle activity,

(ii) the rate of soil movement onto road and pavement surfaces,

(iii) metal inputs to the system resulting from the breakdown of roofing materials,

(iv) the accumulation of material in gully pots and surface depressions and their re-incorporation in runoff,

and (v) the acceptability of Sartor and Boyds washoff equation for simulating pollutant removal from road surfaces especially the constant k.

In conclusion therefore, the outcome of the model indicated that the hypotheses developed concerning the pollution pathways within the catchment were essentially correct, as reasonable agreement was found between the observed and simulated events. The mean, standard deviations and correlation coefficients were within acceptable limits.

The model could provide the foundation for the development of a general conceptual model for simulating the movement of heavy metals and other pollutants through a small catchment. Such a model would provide planners and designers with a useful predictive tool.

Although the nature of the results obtained in the study do not allow a completely confident prediction of the heavy metal pollutants in any catchment, due to their site specific nature, results of this type do allow the designer to establish general trends of behaviour and thus design sewer systems within acceptable limits.

15.7 Overview

It should be noted that the results obtained in this study are site specific and care should be taken when attempting to relate the results to other catchments.

With hindsight it would appear that the goals initially set by the research programme were far too wide ranging. However, it is felt that this thesis will form a source of valuable information to enable more detailed research studies to be carried out into many of the individual topics covered in the thesis.

The research programme is now an ongoing subject and is currently being further researched at the University of Aston in Birmingham. This thesis forming the preliminary study.

APPENDIX A

ANALYTICAL PROCEDURES

A.1 Introduction

The investigation of trace heavy metals in a given medium requires sensitive and precise techniques. Classical methods alone are not of sufficient accuracy to determine very low concentration levels of metal species in the range of parts per million (ppm). Therefore more sensitive instrumental methods have been developed and are now widely used. These highly sensitive techniques normally require samples to be pretreated, usually to eliminate interfering substances and also to bring the elements being studied into the concentration range and chemical state required for the analytical detection system.

In this research project, the determination of low concentration levels for the heavy metals was achieved through the application of the highly sensitive technique of Atomic Absorption Spectrophotometry (AAS). This instrumental detection method was chosen on the grounds of practicability and availability within the research establishment.

When analysing samples for trace metals, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and contaminated laboratory analysis, all are potential sources of contamination. The collection and treatment of the sample prior to analysis therefore requires particular attention. Therefore an intensive washing procedure was carried out on all apparatus, which consisted of soaking in a strong detergent (Decon), washing with tap-water, rinsing with a dilute solution of nitric acid (10% GPR grade), rinsing with EDTA (Ethylene Diamine Tetra Acetic acid) and finally rinsing twice with deionized distilled water and then dried.

There are two basic stages to the Atomic Absorption Spectrophotometric method. Firstly pretreatment, which involves mineralization and solubilization of metals present in samples containing organic fractions. This was achieved by aqua regia acid digestion ($HCl:HNO_3$ 3:1), secondly, metal determination was then conducted by the application of Atomic Absorption Spectrophotometric analysis.

Recommended methods of preparation for runoff samples are not consistent in the literature and in some cases the method of digestion is not specified. There are , however, two widely used procedures which involve digestion with either nitric-hydrofluoric acid (Shaheen (1975) and Analytical Methods for AAS (1971)), or the less time consuming methods using nitric-hydrochloric acid (Pitt and Amy (1973) and Standard Methods EPA (1976)).

Bourcier and Sharma (1980) compared these two most commonly used procedures and concluded that the $HCl - HNO_3$ method of digestion produced results equivalent to the $HF - HNO_3$ method. However, due to the special equipment and additional time necessary for digestion by hydrofluoric acid, the hydrochloric acid technique was recommended as adequate for stormwater analysis. The latter method was therefore adopted for this study. It was also recommended by the Severn Trent Water Authority (Bennett (1982)).

General acid digestion procedures are also available for total elemental analysis in soils and sediments. Various digestion reagents can be used including concentrated HNO_3, HCl-HNO_3, HNO_3-H_2O_2, HCl-HF and HNO_3-$HClO_4$. All are strong oxidizing agents efficient in the digestion of carbonates, phosphates and other constituents. The digestion reagent used for the road sediment and soil samples was that of aqua regia. It was selected for a number of reasons.

(i) It has been used successfully by a number of authors, including Duggan and Williams (1977), Laxen and Harrison (1977), Harrison (1979) and Wilber and Hunter (1975). It was also recommended in the EPA Methods for the Chemical Analysis of Waters and Wastes (1971). Laxen and Harrison (1977) showed that a procedure using concentrated nitic and hydrochloric acids had a high efficiency close to that of nitric/hydrofluoric acid mixture, taken to be the most effective extractant available.

(ii) It was also recommended by JURUE(1983).

(iii) A common reagent was required for the analysis of allsample types and HCl-HNO_3 had already been selected for the stormwater and deposit cannister samples. Hence results from different sample types could be compared.

All acids used were of ARISTAR grade and reagent blanks (controls) for all samples and sample types were prepared in the same manner as the samples, to take into account any metals introduced into the samples from contamination of apparatus or chemicals.

Samples were analysed within the JURUE laboratory which participated in national quality control surveys and were constantly monitored to ensure quality was maintained. All of the techniques used in this research project were standard procedures used in the JURUE laboratory and had previously been tried and tested to check the quality of the results obtained. All methods used were shown to give compatible results when compared with standards obtained from other laboratories.

The samples mentioned in this report were analysed by the same method and so were comparable with each other on that basis. The results were also comparable with other studies which used aqua regia as an acid digestion techique.

Samples were analysed for the total metal analysis of iron, lead, zinc, copper, chromium, nickel and cadmium.

A.2 Analytical Processes for the Pretreatment of Samples

A.2.1 Stormwater Runoff Samples

The behaviour of heavy metals is to a large extent governed by the speciation or chemical form in which the metal may exist. The chemical forms can exist as particulate matter or in a dissolved state. The accepted method for distinguishing between the dissolved and particulate forms in water is by the use of a 0.45 micron membrane filter, and thus dissolved metal solutions consist of a mixture of metal forms < 0.45 micron. The samples in this study were analysed for the total metals between the two states.

A.2.1.1 Dissolved Metals

The unpreserved sample was filtered through a 0.45 micron membrane filter on a buchner filter funnel, with the aid of a small vacuum suction pump. Once all of the solution had been filtered, the filtrate was acidified with 1:1 HNO_3 (50% nitric acid) to pH 2 (approximately 3 ml per litre). This was to prevent the precipitation and absorption of metals in the solution and gave the sample a holding capacity of 6 months (EPA (1971)). The samples were then preconcentrated where necessary by evaporation (boiling) and then transferred to glass sample tubes and stored in the refrigerator prior to direct analysis by AAS.

A.2.1.2 Particulate Metals

The unpreserved sample was filtered through a 0.45 micron membrane filter as above, and the volume of filtrate recorded. The membrane filter was then carefully removed from the funnel with the aid of plastic tweezers, and placed into a kjedahl flask. The flasks were then transferred to the fume cupboard where 10 ml of aqua regia acid was added (2.5 ml HNO_3 and 7.5 ml HCL). The flask was then warmed gently in a rack heater. When dissolution was complete the temperature was increased to digest the material over a period of 2 to 3 hours. The sample was then cooled, filtered, using a Whatman 41 ashless filter paper, and transferred to a suitable volumetric flask (grade A), and the volume adjusted with deionized distilled water to bring the metal concentration to a suitable level for analysis. The samples were then transferred to glass sample tubes and stored in the refrigerator prior to AAS.

A.2.2 Road Sediment and Soil Samples

Road sediment and soil samples collected in the field were returned to the laboratory and placed into labelled aluminium foil bags. The samples were then dried in the oven at 105°C for 24 hours. After drying, they were removed, cooled in a dessicator and each sample was hand ground using a pestle and mortar (in order to obtain a representative sample) so that it passed through a 250 micron stainless steel sieve. To avoid cross contamination at this stage, the pestle, mortar and sieve were thoroughly cleaned and dried between each sample. One gramme of the sample was then accurately weighed (to 3 decimal places) and transferred to a 50 ml kjedahl flask where a few anti-bumping granules were added. In the fume cupboard 10 ml of aqua regia acid were added and the flask placed in a rack heater. The sample was gently heated whilst the green/brown fumes of nitrogen dioxide evolved. The temperature was then increased whilst the sample was digested (2 to 3 hours for the road sediments and 4 to 5 hours for the soils). After digestion the samples were left to cool before being filtered through a Whatman 41 ashless filter paper. Each sample was then transferred to a suitable volumetric flask (grade A) and the volume adjusted with deionized distilled water to give a standard volume. The samples were then further transferred to glass sample tubes and stored in the refrigerator awaiting determination. Samples were diluted wherever necessary using an automatic diluter filled with deionized distilled water.

A.2.3 Deposit Cannister Samples

The samples collected in the field were returned to the laboratory in sealed deposit cannisters. These were analysed immediately on collection.

When the cannister was opened the contents were poured into a 50 ml kjedahl flask. Any insoluble fraction remaining was washed out and the interior of the cannister wiped out using a cellulose ashless filter paper, which was added to the contents of the kjedahl flask. The flask was then placed onto a rack heater, the sample evaporated to near dryness and allowed to cool. Each flask was then transferred to the fume cupboard where 10 ml of aqua regia acid were added, and heated gently until the green/brown fumes of nitrogen dioxide had evolved. The temperature was then slowly increased. After 2 to 3 hours, when all of the organic matter had been digested, the sample was cooled. The flask contents were then washed out and filtered through a Whatman 41 ashless filter paper into a 10 ml grade A volumetric flask and made up to volume with deionized distilled water. The digested samples were subsequently transferred to glass sample tubes and stored in the refrigerator awaiting determination.

A.3 Atomic Absorption Spectrophotometry

The concentration of total metals, iron, lead, zinc, copper, chromium, nickel and cadmium, in all samples were measured on a Perkin Elmer 560 Double Beam Atomic Absorption Spectrophotometer. Conventional flame absorption was employed using a single slot burner head, with a deuterium arc background correction where necessary. The instrument was set up according to the manufacturers recommendations.

The concentrations of the metals in each sample solution were obtained from an absorption/concentration calibration graph, using commercially prepared (BDH chemicals) stock standard solutions (1000 mg/l) of iron, lead, zinc, copper, chromium, nickel and cadmium. Suitable dilutions of the stock solutions were freshly prepared on each day of analysis and refrigerated when not in use. The standards used are given in Table A.1.

Individual hollow cathode lamps were used as radiation sources for each of the metals to be determined. The wavelengths and slit settings used, together with the type of flame employed are given in Table A.2.

Hollow cathode lamp alignment, burner angle, gas flow and nebulizer (sample aspiration rate) were adjusted to achieve maximum sensitivity of the instrument using duplicate standards. The sensitivity and detection limits for this instrument (Perkin Elmer, Model 560) are given in Table A.3, together with the optimum concentration ranges.

The performance and calibration of the instrument was checked by frequent atomization of standards during each analysis run, so that corrections for wavelength drift or lamp/burner misalignment could be made. Finally, results obtained from the calibration graph of absorbance readings, were corrected for sample dilutions.

Metal	Stock Standard Solutions						Linear Range
Fe	5	10	15	30	45	60	5
Pb	10	20	40	60	80	120	20
Zn	1	2	4	6	8	12	1
Cu	2	5	10	15	20	30	5
Cr	5	10	15	30	45	60	25
Ni	1	2	4	8	12	24	2
Cd	0.5	1	2	-	-	-	2

Table A.1 Concentrations of stock standard solutions used in the analysis (mg/l).

Metal	Wavelength (nm)	Slit (nm)	Flame	
Fe	248.3	0.2	N_2O/C_2H_2	oxidizing (lean blue)
Pb	283.3	0.7	Air/C_2H_2	oxidizing (lean blue)
Zn	213.9	0.7	Air/C_2H_2	oxidizing (lean blue)
Cu	324.8	0.7	Air/C_2H_2	oxidizing (lean blue)
Cr	357.9	0.7	N_2O/C_2H_2	reducing (rich yellow)
Ni	232.2	0.7	N_2O/C_2H_2	oxidizing (lean blue)
Cd	228.8	0.7	Air/C_2H_2	oxidizing (lean blue)

Table A.2 Wavelengths, slit settings and flames employed in the analysis.

C_2H_2 = Acetylene : N_2O = Nitrous oxide

Metal	Detection Limit (mg/l)	Sensitivity (mg/l)	Optimum Conc. Range (mg/l)
Fe	0.005	0.1	0.1 - 20
Pb	0.01	0.45	1 - 10
Zn	0.001	0.018	0.1 - 2
Cu	0.002	0.077	0.1 - 10
Cr	0.003	0.078	1 - 200
Ni	0.005	0.14	0.1 - 20
Cd	0.001	0.028	0.1 - 2

Table A.3 Sensitivity and detection limits for the Perkin Elmer Model 560 Atomic Absorption Spectrophotometer (AAS).

APPENDIX B

ROAD DUST ANALYSIS

B.1 Determination of Vehicle Metal Input Rate

A computer program was developed for a BBC Micro which allowed the vehicle metal input rates to be determined through a converging iterative procedure (Hedges (1985)), providing the rate of soil input to the road surface was specified. Essentially the proportion of each metal which could be expected to be present in the road dust was calculated from the known average aerial deposition rate together with the metal input rate calculated from the specified soil input rate and a starting metal input rate from vehicle activity. This was subsequently compared with the actual proportion found in the road dust.

Initially the proportion of lead was compared, the level of vehicle lead was then adjusted until an agreement to a specified level of accuracy was obtained. Once agreement for lead was obtained, the next metal was considered and vehicle metal input adjusted if necessary, since any adjustment would alter the proportion of lead present. As soon as one metal occurred the procedure had to be re-started with lead. The procedure was continued until convergence, when the calculated proportion of each metal in road dust matched analysis results to the specified accuracy (0.01%).

It was found that if all six non-ferrous metals were considered, some very high levels of lead vehicle deposition rate was achieved. These were attributed to balancing cadmium levels, which although very small were considered to be in error for the topsoil. As a result cadmium was removed from the analysis and when the remaining five metals were used alone the results obtained were consistent with those quoted in the literature.

B.1.2 Relationships between Vehicle Metal Input to the Road Surface and Soil in Road Dust

Through the application of the program a curve was plotted which showed the relationship between the input rate to the road from vehicle activity and soil accumulation rate for lead, zinc, copper, chromium and nickel. Although the literature search failed to reveal any one specific metal vehicular input rate, upper and lower bands for lead and zinc have been identified. These when added to the relationships for lead, confirmed that the values attained were feasible and provided an upper cut off limit. The upper band for Chelmsley Wood was provided by lead, when the range quoted by Shaheen (1975) of 4 to 11 mg/veh km, was taken. The minimum lead input rate, 6.05 mg/veh km was higher than that of Shaheen, but was thought to be feasible. The upper limit of 11 mg/veh km gives a maximum possible soil input rate of 1.1 gm/sq m per day. The rate of zinc input to the road surface fell between the two bands obtained with the literature search. Thus a maximum lead vehicular input rate limits the soil input rate to the road surface to 1.1 gm/sq m per day, which in turn gave possible ranges of individual metal input as shown in Table B.1.

With a view for fixing a vehicular metal input rate, a conceptual model of the catchment was built.

The model was calibrated on lead and from this a vehicle lead deposition rate of 7 mg/veh km was obtained, hence fixing the soil accumulation rate on roads and pavements to 0.25 gm/sq m per day, which was subsequently used in the model (see Figure 14.3).

METAL	SOIL INPUT TO ROAD SURFACE (gm/sq m per day)	
	0.00	1.1
Lead	6.05	11
Zinc	1.925	2.57
Copper	0.565	0.74
Chromium	0.31	0.175
Nickel	0.175	0.205

Table B.1 Vehicle metal input rate direct to road surface in mg/veh km for minimum and maximum soil input rates.

APPENDIX C

The following is a listing of the deposit cannister, road sediment, soil and stormwater quality data obtained for the sampling period July 1983 to July 1984.

Deposit Cannister Data (total µg)

Date	Location	Iron	Lead	Zinc	Copper	Chromium	Nickel	Cadmium
83/08/17	p1	135.20	7.00	13.10	1.78	0.00	1.77	0.14
83/08/17	p2	141.00	23.00	11.60	4.13	0.00	3.24	0.76
83/08/17	p4	233.00	7.00	24.10	4.25	0.00	0.00	0.56
83/08/17	p6	110.30	7.00	16.90	5.40	0.00	0.00	0.06
83/08/17	p7	105.30	7.00	9.30	3.52	0.00	0.00	0.53
83/08/17	p8	185.40	9.00	12.60	5.86	0.00	1.92	0.14
83/08/17	p9	56.70	6.00	5.10	3.20	0.00	0.00	0.08
83/08/17	p14	196.30	3.00	10.90	2.93	0.00	0.00	0.00
83/08/17	p15	104.70	7.00	8.00	3.11	0.00	3.75	0.09
83/08/17	p16	139.10	5.00	10.10	3.15	0.00	0.00	0.08
83/08/17	p18	131.10	6.00	9.90	2.36	0.00	0.00	0.00
83/08/17	p19	416.40	4.00	7.40	6.86	0.00	0.00	0.00
83/08/17	p21	113.90	4.00	8.00	2.36	0.00	0.00	0.44
83/08/17	p22	77.80	3.00	6.50	3.86	0.00	0.00	0.00
83/09/14	p1	63.00	9.20	8.30	2.10	0.00	0.00	0.88
83/09/14	p2	168.90	17.30	14.10	4.90	0.00	0.00	0.22
83/09/14	p4	114.00	10.70	12.30	3.30	0.00	0.00	0.32
83/09/14	p6	57.10	7.20	13.10	2.30	0.00	0.00	0.00
83/09/14	p7	113.70	7.40	13.00	2.00	0.00	0.00	0.27
83/09/14	p8	110.80	6.80	13.00	5.10	0.00	0.00	0.45
83/09/14	p9	96.20	7.40	9.20	3.80	0.00	0.00	0.00
83/09/14	p14	92.60	4.60	12.80	4.40	0.00	0.00	0.42
83/09/14	p15	138.20	14.60	13.40	4.60	0.00	0.00	0.00
83/09/14	p16	121.50	10.40	13.10	3.10	0.00	0.00	0.45
83/09/14	p18	175.90	9.40	13.40	5.30	0.00	0.00	0.46
83/09/14	p21	133.60	8.00	12.00	4.90	0.00	0.00	0.00
83/10/12	p1	22.90	9.60	5.30	1.00	0.00	0.00	0.30
83/10/12	p2	78.00	23.10	9.70	1.40	0.00	0.00	0.00
83/10/12	p5	89.00	8.00	5.20	1.60	0.00	0.00	0.10
83/10/12	p6	77.00	8.80	6.40	1.60	0.00	0.00	0.00
83/10/12	p7	90.00	6.90	7.00	1.10	0.00	0.00	0.10
83/10/12	p8	57.00	4.20	4.90	1.00	0.00	0.00	0.20
83/10/12	p9	93.00	11.60	5.60	1.20	0.00	0.00	0.00
83/10/12	p15	108.00	10.80	30.10	4.50	0.00	0.00	0.00
83/10/12	p16	96.00	5.50	10.10	3.60	0.00	0.00	0.00
83/10/12	p19	130.00	7.70	8.00	2.80	0.00	0.00	0.30
83/10/12	c1	0.00	0.00	0.00	0.00	0.00	0.00	0.00
83/11/09	p1	35.00	12.50	9.00	2.20	0.10	2.00	0.00
83/11/09	p2	93.00	12.40	11.90	2.70	0.20	5.00	0.10
83/11/09	p6	20.00	9.40	10.40	1.30	0.40	2.00	0.00
83/11/09	p7	62.00	7.80	9.70	1.80	0.50	0.00	0.00
83/11/09	p8	44.00	6.60	8.20	1.60	0.60	0.00	0.00
83/11/09	p9	49.00	6.10	6.80	2.80	1.40	0.00	0.00
83/11/09	p12	62.00	8.20	11.10	2.90	1.20	0.00	0.30
83/11/09	p15	62.00	12.10	18.30	2.30	0.90	0.00	0.10
83/11/09	p16	76.00	5.30	9.90	1.70	1.90	0.00	0.00
83/11/09	p22	15.00	3.10	7.00	1.50	0.20	1.00	0.20
83/12/07	p1	36.50	7.10	6.00	1.60	0.00	0.00	0.19
83/12/07	p2	60.20	11.70	8.40	2.00	0.10	0.80	0.53
83/12/07	p4	42.80	9.10	7.30	1.40	0.00	1.10	0.00
83/12/07	p5	40.10	6.10	6.40	1.20	0.00	2.20	0.07
83/12/07	p6	36.70	4.40	7.00	1.10	0.00	1.50	0.00
83/12/07	p7	56.20	6.20	7.90	1.70	0.20	0.60	0.23

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Deposit Cannister Data (total µg)

Date	Location	Iron	Lead	Zinc	Copper	Chromium	Nickel	Cadmium
83/12/07	p8	44.60	4.80	7.50	1.20	0.00	2.00	0.52
83/12/07	p9	93.10	7.20	9.00	1.90	0.00	1.10	0.53
83/12/07	p12	30.70	8.20	6.70	1.20	0.40	2.70	0.22
83/12/07	p15	52.70	11.30	7.80	3.50	0.00	2.20	0.86
83/12/07	p16	64.80	5.60	9.00	3.80	0.50	2.90	0.60
83/12/07	p21	57.60	4.90	9.30	2.70	0.00	0.80	0.59
84/01/04	p1	28.60	6.30	5.90	1.10	0.00	0.80	0.00
84/01/04	p2	55.70	6.50	6.90	1.50	0.00	1.30	0.26
84/01/04	p4	36.00	6.80	4.50	2.10	0.00	1.60	0.71
84/01/04	p5	29.70	5.50	3.00	1.00	0.20	0.00	0.89
84/01/04	p7	61.90	5.20	4.80	1.20	0.00	0.00	0.15
84/01/04	p8	40.10	0.20	4.70	1.70	1.00	0.80	0.64
84/01/04	p9	40.50	8.20	3.00	0.70	0.30	0.00	0.45
84/01/04	p12	74.60	10.20	4.00	1.20	0.80	1.70	0.00
84/01/04	p15	52.00	9.70	3.80	1.20	0.30	1.30	0.40
84/01/04	p16	43.60	3.70	5.40	0.90	1.40	0.70	0.32
84/01/04	p21	51.20	7.70	6.50	1.50	0.50	2.00	0.00
84/02/01	p1	42.50	7.30	10.70	1.90	0.00	1.09	0.00
84/02/01	p2	89.20	10.20	11.30	2.10	0.00	1.27	0.00
84/02/01	p4	54.10	6.70	9.50	2.30	0.30	1.52	0.00
84/02/01	p5	45.90	7.00	8.10	1.90	1.00	0.00	0.02
84/02/01	p8	79.90	7.30	13.50	2.20	0.70	1.75	0.08
84/02/01	p9	54.90	9.20	8.30	1.00	0.00	0.00	0.16
84/02/01	p12	48.10	9.10	16.50	1.70	0.90	1.73	0.09
84/02/01	p15	2.80	10.40	10.40	1.90	0.10	2.60	0.68
84/02/01	p16	49.80	6.70	10.00	3.20	0.50	3.11	0.15
84/02/01	p21	77.60	7.90	11.90	2.80	1.00	4.53	0.55
84/02/29	p1	74.40	9.40	14.30	3.60	1.10	1.58	0.00
84/02/29	p2	195.90	43.20	17.00	4.70	0.70	1.06	0.00
84/02/29	p4	68.90	9.30	14.50	3.00	0.10	0.40	0.21
84/02/29	p5	58.60	7.40	10.90	2.30	0.40	1.32	0.11
84/02/29	p7	95.10	6.50	11.90	2.70	0.00	1.16	0.37
84/02/29	p8	136.20	6.30	17.80	3.10	0.50	0.63	0.60
84/02/29	p9	65.60	7.00	12.20	1.90	1.40	0.00	0.27
84/02/29	p12	62.60	9.20	13.00	2.00	1.40	0.00	0.51
84/02/29	p15	90.40	11.40	13.20	4.60	1.30	0.60	0.00
84/02/29	p16	126.30	6.40	12.30	3.60	0.40	0.77	0.13
84/02/29	p21	136.70	9.00	16.80	3.20	0.50	1.44	0.00
84/03/28	p1	88.90	13.00	10.70	3.40	0.30	1.50	0.14
84/03/28	p2	152.00	34.00	16.20	4.00	1.10	0.00	0.12
84/03/28	p4	105.80	13.00	11.60	3.30	0.60	0.00	0.39
84/03/28	p7	109.90	10.00	12.80	2.30	0.60	0.00	0.21
84/03/28	p8	142.20	13.00	18.10	3.80	1.00	0.00	0.23
84/03/28	p9	79.20	11.00	8.30	2.60	1.10	0.40	0.03
84/03/28	p12	81.90	11.00	9.80	1.90	0.30	0.00	0.00
84/03/28	p16	103.40	5.00	11.70	1.90	0.30	0.40	0.04
84/03/28	p21	181.00	8.00	15.80	4.20	0.00	0.00	0.13
84/04/25	p1	63.40	6.00	7.20	2.00	1.20	1.52	0.41
84/04/25	p2	108.30	15.00	13.10	3.20	1.20	2.49	0.51
84/04/25	p4	78.80	6.00	8.70	2.10	1.00	1.49	0.63
84/04/25	p5	69.90	8.00	8.90	1.60	1.20	1.72	0.19
84/04/25	p7	83.50	5.00	7.60	1.60	1.00	1.56	0.55
84/04/25	p8	125.30	7.00	9.90	2.40	1.60	0.91	0.51

Deposit Cannister Data (total µg)

Date	Location	Iron	Lead	Zinc	Copper	Chromium	Nickel	Cadmium
84/04/25	p9	40.50	5.00	7.40	1.40	0.30	0.54	0.12
84/04/25	p12	51.80	4.00	9.10	1.90	0.00	0.00	0.27
84/04/25	p15	93.50	9.00	10.00	2.50	1.00	0.00	0.93
84/04/25	p16	112.70	5.00	10.30	2.50	0.50	0.00	0.30
84/04/25	p21	105.00	5.00	9.40	2.40	0.70	0.31	0.21
84/05/23	p1	109.70	12.00	6.10	1.50	0.70	2.00	1.06
84/05/23	p2	129.20	21.00	6.30	1.50	1.80	0.00	1.02
84/05/23	p4	104.10	12.00	8.50	2.00	0.30	0.00	1.11
84/05/23	p5	100.50	12.00	6.70	2.00	0.80	4.00	1.89
84/05/23	p7	131.50	5.00	9.10	1.60	0.70	0.00	1.46
84/05/23	p8	156.60	9.00	12.00	2.90	0.60	2.00	2.00
84/05/23	p9	112.60	6.00	5.20	1.00	0.60	1.00	3.85
84/05/23	p12	66.60	9.00	4.50	0.80	1.00	0.00	0.17
84/05/23	p15	115.80	11.00	8.30	3.40	0.60	1.00	0.36
84/05/23	p16	352.00	10.00	9.10	3.60	0.80	0.00	0.12
84/05/23	p21	202.20	7.00	9.40	2.50	0.60	1.00	0.88
84/06/20	p1	75.90	10.00	6.10	1.70	0.40	1.50	0.31
84/06/20	p2	155.10	40.00	8.20	2.40	0.60	2.30	0.00
84/06/20	p4	74.90	9.00	5.60	11.50	0.60	2.79	0.00
84/06/20	p5	85.80	9.00	5.00	1.80	0.50	2.24	0.28
84/06/20	p7	58.10	5.00	4.60	1.20	0.40	0.34	0.06
84/06/20	p8	80.00	7.00	7.60	1.70	0.10	0.83	0.00
84/06/20	p12	803.80	11.00	6.90	2.70	0.90	1.17	0.32
84/06/20	p16	117.20	5.00	6.60	1.70	0.30	6.04	0.00
84/06/20	p21	139.10	7.00	7.20	2.00	0.60	0.41	1.42
84/07/18	p1	254.40	13.00	10.40	3.50	2.30	5.92	0.04
84/07/18	p2	94.10	8.00	6.70	2.50	0.30	2.48	0.36
84/07/18	p4	110.40	8.00	6.90	2.50	0.90	2.61	0.37
84/07/18	p5	57.20	7.00	4.90	1.70	0.40	0.00	0.18
84/07/18	p7	73.60	5.00	6.60	1.70	1.00	1.08	0.17
84/07/18	p8	107.50	5.00	9.50	2.50	0.70	0.13	0.37
84/07/18	p9	44.50	4.00	5.00	1.30	0.50	3.57	0.06
84/07/18	p12	93.10	9.00	9.00	2.20	0.70	1.04	0.34
84/07/18	p15	85.50	9.00	7.80	2.60	0.60	3.36	1.18
84/07/18	p16	103.80	5.00	6.30	3.20	0.80	1.26	0.40
84/07/18	p21	116.60	5.00	9.80	3.30	1.00	2.56	0.37

Road Sediment Data (mg/kg)

Date	Location	Iron	Lead	Zinc	Copper	Chromium	Nickel	Cadmium
83/07/26	1	20710.00	950.00	280.00	66.55	36.85	25.75	1.36
83/07/26	2	22600.00	1550.00	400.00	150.00	47.20	34.00	2.92
83/07/26	3	18655.00	494.00	195.00	67.15	51.90	24.80	2.40
83/07/26	4	25325.00	950.00	285.00	139.30	62.45	96.00	1.61
83/07/26	5	4675.00	2350.00	375.00	155.50	56.30	62.25	2.97
83/07/26	6	28980.00	2550.00	475.00	174.65	55.05	62.00	2.31
83/07/26	7	19195.00	550.00	230.00	121.80	31.40	39.40	2.15
83/07/26	8	18145.00	564.00	270.00	94.30	28.65	44.30	1.75
83/07/26	9	24410.00	1400.00	195.00	111.85	36.20	56.70	1.89
83/07/26	10	17515.00	1250.00	250.00	94.95	49.15	36.10	1.66
83/07/26	11	20240.00	1200.00	310.00	144.05	86.20	34.16	1.72
83/07/26	12	23100.00	1850.00	390.00	101.65	54.10	40.70	1.55
83/07/26	13	15260.00	432.50	226.25	549.65	64.55	26.65	1.15
83/07/26	14	13415.00	61.00	95.00	49.10	106.00	31.95	0.99
83/07/26	15	24080.00	1400.00	340.00	102.70	80.10	59.75	1.79
83/07/26	16	21725.00	365.00	320.00	102.95	69.30	71.50	4.76
83/07/26	17	19850.00	850.00	350.00	112.25	57.40	56.95	2.13
83/07/26	18	8970.00	486.00	315.00	65.35	25.90	45.50	2.35
83/07/26	19	24525.00	800.00	205.00	95.10	40.50	47.25	0.95
83/07/26	20	14770.00	254.50	210.00	69.10	22.80	27.85	1.54
83/07/26	21	21930.00	1500.00	335.00	86.00	160.60	45.25	1.63
83/07/26	22	19105.00	522.50	290.00	57.05	237.00	45.45	2.48
83/07/26	23	12895.00	277.00	70.00	49.10	36.55	51.15	2.61
83/07/26	24	13905.00	775.00	425.00	143.15	37.15	34.95	1.54
83/08/09	1	21424.00	1099.00	479.50	108.90	40.05	40.65	2.81
83/08/09	2	44014.00	3699.00	834.50	254.75	60.45	44.05	2.66
83/08/09	3	20259.00	515.00	249.50	38.40	39.75	21.30	0.75
83/08/09	4	29509.00	1299.00	394.50	249.75	49.60	54.60	1.00
83/08/09	5	31974.00	2749.00	564.50	209.75	44.55	56.35	2.27
83/08/09	6*	31494.00	2924.00	674.50	229.75	54.98	672.40	3.28
83/08/09	7	26029.00	949.00	399.50	151.10	33.05	49.20	1.98
83/08/09	8	20134.00	534.00	374.50	70.00	24.80	30.80	4.08
83/08/09	9	30704.00	1599.00	374.50	224.75	46.15	734.90	1.42
83/08/09	10	24629.00	1299.00	294.50	96.20	27.80	25.90	3.35
83/08/09	11	26514.00	1549.00	554.50	224.75	118.05	52.00	2.07
83/08/09	12	20614.00	1299.00	624.50	74.05	74.80	23.30	1.39
83/08/09	13	19069.00	449.50	494.50	389.75	58.00	27.30	1.97
83/08/09	14	30954.00	437.00	454.50	160.30	66.30	50.25	4.83
83/08/09	15	33794.00	2349.00	609.50	144.90	50.35	34.80	1.95
83/08/09	16	20339.00	121.00	279.50	60.50	92.75	58.95	1.71
83/08/09	17	25784.00	799.00	419.50	106.95	38.65	51.25	2.11
83/08/09	18	20014.00	559.50	354.50	81.50	26.80	33.15	1.73
83/08/09	19	20964.00	949.00	359.50	95.80	31.10	52.35	1.34
83/08/09	20	18294.00	305.50	229.50	83.05	19.80	28.25	1.43
83/08/09	21	30179.00	1399.00	619.50	204.75	118.60	55.60	2.72
83/08/09	22	30854.00	616.50	379.50	84.50	176.50	34.65	1.52
83/08/09	23	14354.00	355.50	299.50	46.10	28.65	42.25	1.88
83/08/09	24	12759.00	119.00	709.50	36.70	25.20	30.70	2.42
83/08/23	1	25465.00	1300.00	495.00	88.70	38.65	44.60	2.46
83/08/23	2	29390.00	1850.00	535.00	144.50	44.40	60.45	2.57
83/08/23	3	20980.00	494.00	240.00	65.50	37.95	29.90	1.05
83/08/23	4	21740.00	587.50	240.00	54.80	21.90	21.40	1.46
83/08/23	5	25255.00	950.00	440.00	85.10	33.50	53.30	5.05
83/08/23	6	27250.00	2850.00	570.00	117.25	35.30	56.70	3.43

Road Sediment Data (mg/kg)

Date	Location	Iron	Lead	Zinc	Copper	Chromium	Nickel	Cadmium
83/08/23	7	26325.00	700.00	450.00	135.10	33.65	57.45	1.94
83/08/23	8	15970.00	373.00	335.00	48.10	22.40	32.15	2.31
83/08/23	9	20815.00	1200.00	205.00	49.95	21.50	24.30	0.71
83/08/23	10	23990.00	1400.00	345.00	99.85	33.75	35.55	2.09
83/08/23	11	20105.00	850.00	315.00	64.90	37.90	29.30	1.58
83/08/23	12	14145.00	1850.00	990.00	110.35	56.60	41.15	2.24
83/08/23	13	50550.00	950.00	1520.00	1295.00	104.85	91.25	5.58
83/08/23	14	28605.00	292.50	340.00	88.30	43.20	59.38	4.94
84/08/23	15	34600.00	1700.00	505.00	105.80	50.50	58.60	1.81
83/08/23	16	22600.00	248.00	365.00	61.30	36.95	41.85	3.92
83/08/23	17*	22552.00	775.00	425.50	92.55	32.93	43.60	2.41
83/08/23	18	18560.00	457.50	325.00	65.35	24.20	35.00	2.52
83/08/23	19	20940.00	535.50	225.00	39.10	21.90	28.25	1.35
83/08/23	20	22555.00	336.50	230.00	49.10	18.10	32.05	1.33
83/08/23	21	26625.00	1250.00	465.00	94.85	89.40	52.10	1.89
83/08/23	22	22195.00	850.00	425.00	130.75	81.40	45.05	2.87
83/08/23	23	54350.00	1000.00	330.00	82.60	36.25	43.25	3.59
83/08/23	24	11390.00	106.00	420.00	32.45	23.00	36.45	2.72
83/09/05	1	29840.00	1450.00	565.00	200.00	51.50	31.25	2.42
83/09/05	2	27680.00	1700.00	625.00	93.75	35.85	10.80	2.26
83/09/05	3	24960.00	649.00	330.00	76.50	47.50	11.70	2.33
83/09/05	4	23000.00	1100.00	455.00	100.65	38.85	21.95	1.16
83/09/05	5	30000.00	2100.00	620.00	138.95	46.40	23.15	7.91
83/09/05	6	26620.00	1700.00	485.00	152.00	35.35	24.10	1.48
83/09/05	7	23180.00	534.00	355.00	95.50	25.65	8.85	2.08
83/09/05	8	22050.00	394.50	335.00	71.75	23.70	19.00	4.20
83/09/05	9	32880.00	2000.00	380.00	108.55	34.50	19.85	1.67
83/09/05	10	26660.00	1200.00	380.00	118.00	36.40	20.45	1.13
83/09/05	11	25780.00	1400.00	500.00	117.85	79.35	16.35	2.11
83/09/05	12	25990.00	2050.00	945.00	149.35	80.45	25.75	3.05
83/09/05	13	20910.00	337.50	690.00	700.00	48.20	12.15	1.92
83/09/05	14	30480.00	323.50	415.00	130.60	46.50	30.30	4.46
83/09/05	15	31110.00	1800.00	520.00	154.70	51.15	20.95	2.30
83/09/05	16*	27492.00	342.50	402.50	90.15	52.00	20.67	5.08
83/09/05	17	28880.00	1200.00	530.00	153.75	44.75	20.15	3.38
83/09/05	18	21875.00	505.50	430.00	65.10	24.25	13.50	2.35
83/09/05	19	26090.00	900.00	370.00	72.00	28.25	14.75	1.66
83/09/05	20	22955.00	318.50	310.00	68.65	44.80	14.45	1.57
83/09/05	21	30765.00	1450.00	610.00	275.00	74.05	29.50	3.22
83/09/05	22	18885.00	550.00	305.00	73.85	151.30	19.45	2.12
83/09/05	23	39560.00	1250.00	535.00	123.20	43.15	21.95	3.91
83/09/05	24	30570.00	1700.00	520.00	200.00	46.60	20.05	2.74
83/09/26	1	20900.00	1150.00	460.00	100.00	33.10	32.25	2.48
83/09/26	2	26345.00	1500.00	625.00	102.00	37.40	35.10	2.13
83/09/26	3	24145.00	800.00	335.00	100.00	46.90	27.00	1.75
83/09/26	4	20565.00	750.00	345.00	76.50	32.20	27.20	1.36
83/09/26	5	29720.00	1700.00	455.00	126.00	45.30	45.25	1.57
83/09/26	6	28730.00	2250.00	620.00	156.50	41.40	49.90	2.34
83/09/26	7	13380.00	587.00	310.00	88.00	21.00	28.95	1.72
83/09/26	8	12520.00	257.00	245.00	41.00	15.60	18.20	2.14
83/09/26	9	20525.00	1150.00	330.00	101.00	28.60	26.60	1.91
83/09/26	10	18885.00	1100.00	280.00	104.00	26.50	24.80	0.96
83/09/26	11	22125.00	1200.00	480.00	96.50	72.70	38.95	2.77
83/09/26	12	20100.00	1350.00	645.00	87.00	65.70	26.70	2.15

Road Sediment Data (mg/kg)

Date	Location	Iron	Lead	Zinc	Copper	Chromium	Nickel	Cadmium
83/09/26	13	23085.00	470.50	600.00	443.50	64.60	29.30	1.49
83/09/26	14	28660.00	309.50	465.00	122.00	50.40	65.50	5.78
83/09/26	15	28195.00	1000.00	340.00	99.00	54.80	36.30	1.31
83/09/26	16	36987.00	363.00	330.00	188.00	53.20	59.10	5.60
83/09/26	17	17050.00	1000.00	455.00	89.50	32.30	35.30	2.50
83/09/26	18	20360.00	548.00	270.00	83.50	22.70	24.95	1.31
83/09/26	19	19925.00	606.50	375.00	48.00	32.50	32.00	1.76
83/09/26	20	13055.00	114.00	210.00	22.50	16.90	16.10	0.96
83/09/26	21	22750.00	850.00	420.00	93.00	119.10	32.10	1.52
83/09/26	22	20615.00	545.50	335.00	79.50	137.20	25.95	2.47
83/09/26	23	29635.00	1200.00	3420.00	184.50	40.40	39.50	9.23
83/09/26	24	27630.00	1600.00	510.00	112.50	41.60	42.90	1.78
83/10/12	1	17625.00	965.63	609.37	141.37	47.75	48.75	1.38
83/10/12	2	21781.25	715.63	486.25	157.75	47.25	40.25	1.00
83/10/12	3	16968.75	512.50	402.50	120.37	62.00	45.00	0.88
83/10/12	4	16875.00	434.37	402.50	140.37	35.75	55.00	1.25
83/10/12	5	18406.25	525.00	443.13	116.50	33.63	57.50	1.25
83/10/12	6	1684[illegible].75	928.13	364.37	126.25	38.50	43.75	1.38
83/10/12	7	10406.25	237.50	230.63	39.37	16.63	17.50	1.25
83/10/12	8	15375.00	246.87	253.75	60.12	20.87	27.50	0.75
83/10/12	9	19031.25	887.50	424.37	119.50	33.00	45.00	0.75
83/10/12	10	17312.50	650.00	270.00	83.87	26.00	40.00	0.63
83/10/12	11	14093.75	934.37	687.50	114.75	80.37	43.75	1.75
83/10/12	12	13906.25	1000.00	751.25	134.62	62.50	48.75	2.38
83/10/12	13	13906.25	478.13	737.50	737.50	85.75	52.50	1.25
83/10/12	14	14843.75	290.63	315.63	134.63	48.37	56.25	2.38
83/10/12	15	15437.50	684.37	372.50	155.50	86.75	61.25	0.75
83/10/12	16	16218.75	218.75	262.50	75.50	49.50	47.50	1.38
83/10/12	17	12812.50	62.50	380.63	61.13	30.25	41.25	1.63
83/10/12	18	11437.50	425.00	293.13	62.87	30.37	25.00	0.88
83/10/12	19	13031.25	509.37	360.63	76.87	36.25	35.00	1.00
83/10/12	20	6093.75	53.13	90.63	19.50	13.00	10.00	0.50
83/10/12	21	11656.25	196.87	308.75	57.87	100.00	23.75	0.63
83/10/12	22	10531.25	400.00	318.13	46.25	137.50	22.50	0.88
83/10/12	23	7937.50	221.87	268.13	74.37	26.13	38.75	1.63
83/10/12	24	12031.25	418.75	326.25	68.50	30.62	42.50	0.88
83/11/09	1	31859.37	1221.87	1993.13	148.13	61.13	57.50	1.63
83/11/09	2	24562.50	1196.87	418.13	129.50	52.87	28.75	1.13
83/11/09	3	37734.37	521.87	217.50	65.50	20.75	21.25	0.75
83/11/09	4	9740.63	831.25	378.13	80.75	35.37	43.75	0.88
83/11/09	5	10165.63	743.75	406.63	94.13	39.50	36.25	0.88
83/11/09	6	9950.00	1200.00	486.25	120.00	50.25	42.50	1.13
83/11/09	7	5531.25	162.50	187.50	47.37	18.63	17.50	0.63
83/11/09	8	9803.13	328.13	374.75	102.63	31.13	37.50	1.00
83/11/09	9	14393.75	443.75	246.25	93.87	34.63	30.00	0.50
83/11/09	10	14534.37	787.50	221.87	94.63	44.50	30.00	0.75
83/11/09	11	18768.75	706.25	269.37	60.50	51.25	17.50	0.50
83/11/09	12	17952.50	1459.37	1196.87	187.25	106.25	73.75	3.63
83/11/09	13	10343.75	231.25	312.50	103.50	42.87	15.00	0.63
83/11/09	14	19765.63	268.75	325.62	122.00	69.25	60.00	1.75
83/11/09	15	24606.25	1278.13	641.25	157.25	77.12	57.50	1.50
83/11/09	16	24881.25	240.63	306.25	219.13	55.50	39.75	2.63
83/11/09	17	15668.75	437.50	253.75	128.87	76.25	30.00	1.50
83/11/09	18	21812.50	468.75	247.50	160.50	39.50	53.75	1.50

Road Sediment Data (mg/kg)

Date	Location	Iron	Lead	Zinc	Copper	Chromium	Nickel	Cadmium
83/11/09	19	15975.00	275.00	550.00	44.13	37.37	27.50	0.75
83/11/09	20	11315.63	46.87	197.50	42.50	21.75	25.00	0.63
83/11/09	22	11137.50	703.13	503.75	118.63	121.87	35.00	1.00
83/11/09	23	6253.13	371.87	290.62	52.13	37.50	28.75	0.63
83/11/09	24	12884.37	584.37	469.37	95.00	40.50	43.75	1.13
83/12/07	1	25090.00	2115.00	1107.50	182.00	65.50	59.00	2.50
83/12/07	2	26152.50	2945.00	722.50	198.00	65.00	64.00	3.75
83/12/07	4	18902.50	1170.00	593.00	157.50	51.50	62.50	5.00
83/12/07	5	27477.50	2610.00	587.50	266.00	69.50	72.00	2.45
83/12/07	6	24702.50	3605.00	602.50	146.00	49.00	57.00	4.00
83/12/07	7	10290.00	399.50	274.50	51.00	30.00	18.00	5.65
83/12/07	8	19527.50	755.50	463.00	90.00	50.50	46.50	7.65
83/12/07	9	23277.50	1945.00	492.50	190.50	39.00	42.50	3.70
83/12/07	12	10427.50	688.00	358.00	52.50	41.50	28.50	1.75
83/12/07	14	48002.50	462.50	346.50	105.50	94.00	91.50	7.90
83/12/07	16	30965.00	372.00	341.00	174.50	87.00	64.00	4.30
83/12/07	18	17865.00	563.50	417.50	51.50	30.00	25.50	1.40
83/12/07	19	23352.50	305.50	472.50	83.00	43.00	33.00	2.35
83/12/07	21	22702.50	2500.00	437.00	182.50	153.50	42.00	0.95
84/01/04	1	29901.00	1043.50	561.50	134.00	57.00	36.50	4.50
84/01/04	2	35401.00	1809.00	735.50	191.00	68.50	52.00	4.35
84/01/04	4	18201.00	978.50	468.00	86.50	40.50	50.00	2.35
84/01/04	5	17588.50	1414.00	445.00	107.00	41.00	44.00	2.50
84/01/04	7	18126.00	340.00	322.50	85.50	104.00	29.00	2.50
84/01/04	8	14463.50	646.50	506.00	123.50	45.50	34.00	4.20
84/01/04	9	11551.00	278.50	155.00	23.00	20.50	3.50	1.95
84/01/04	12	23108.50	927.00	362.00	252.00	54.50	9.50	2.05
84/01/04	15	661.00	1004.50	357.00	87.50	19.50	29.00	0.60
84/01/04	16	3813.50	511.00	503.50	108.50	16.50	46.50	5.80
84/01/04	21	18613.50	997.00	228.50	166.50	34.50	5.50	2.86
84/02/01	1	29762.00	1858.50	727.00	205.00	68.00	65.25	1.90
84/02/01	2	23724.50	2106.00	819.50	285.50	73.50	62.40	6.15
84/02/01	4	21567.00	1436.00	572.00	143.00	60.00	60.15	2.60
84/02/01	5	25249.50	1783.50	602.50	207.00	64.00	59.20	2.50
84/02/01	7	18824.50	763.50	298.50	75.00	36.50	36.70	1.90
84/02/01	8	14242.00	554.50	363.50	57.00	35.50	34.90	1.65
84/02/01	9	16349.50	504.00	230.00	94.00	39.50	20.40	0.90
84/02/01	12	21562.00	1118.50	572.00	124.50	78.50	55.80	2.55
84/02/01	15	18044.50	883.50	527.50	148.00	60.00	60.05	2.60
84/02/01	16	25637.00	505.50	428.50	102.50	76.00	55.85	5.05
84/02/01	21	22062.00	1006.50	462.50	91.50	128.50	57.70	1.85
84/02/29	1	17323.00	775.00	368.50	92.00	38.00	31.10	2.00
84/02/29	2	25093.00	1412.50	827.50	181.00	64.50	48.60	2.00
84/02/29	4	19680.50	942.50	547.50	124.50	62.50	56.15	0.00
84/02/29	5	20680.50	1192.50	480.00	336.00	61.50	64.55	2.25
84/02/29	7	25368.00	920.00	491.50	150.50	84.50	41.60	0.00
84/02/29	8	13525.50	295.50	253.50	43.00	27.00	22.05	1.85
84/02/29	9	15993.00	512.00	232.00	100.50	44.00	40.90	3.95
84/02/29	12	16580.50	804.00	544.00	116.50	58.50	31.00	2.75
84/02/29	15	22718.00	995.00	494.00	148.50	71.50	53.45	1.85
84/02/29	16	21118.00	324.00	410.50	76.50	50.00	41.45	3.20
84/02/29	21	19518.00	765.00	365.00	87.00	115.50	29.00	1.65
84/03/28	1	19766.00	1515.00	576.00	150.50	70.50	48.00	4.25
84/03/28	2	18066.00	1645.00	566.00	148.50	57.50	34.00	2.65

Road Sediment Data (mg/kg)

Date	Location	Iron	Lead	Zinc	Copper	Chromium	Nickel	Cadmium
84/03/28	4	14341.00	1060.00	498.00	203.50	41.00	35.50	0.90
84/03/28	5	18328.50	1740.00	436.50	159.50	45.00	33.50	3.70
84/03/28	7	13016.00	525.00	258.50	61.50	24.00	11.00	3.75
84/03/28	8	8453.50	350.00	290.00	55.00	25.50	14.50	5.10
84/03/28	9	15153.50	850.00	254.50	140.50	35.50	20.00	0.55
84/03/28	12	13078.50	1035.00	491.00	97.50	63.00	24.00	5.50
84/03/28	15	19953.50	1290.00	425.50	169.00	56.50	44.50	5.05
84/03/28	16	16578.50	320.00	244.00	82.00	44.50	28.00	3.25
84/03/28	21	16341.00	735.00	427.00	174.50	82.50	42.00	2.85
84/04/25	1	23098.00	1050.00	593.00	184.00	46.50	51.90	0.00
84/04/25	2	24623.00	1465.00	459.00	162.50	55.50	59.20	0.00
84/04/25	4	21010.50	1655.00	603.00	154.00	42.50	45.60	0.70
84/04/25	5	23785.50	1600.00	428.00	142.00	47.50	59.90	0.00
84/04/25	7	17085.50	610.00	213.00	58.50	30.00	22.85	0.00
84/04/25	8	12035.50	520.00	353.50	66.00	23.00	30.40	2.75
84/04/25	9	16910.50	800.00	201.50	99.50	29.00	21.00	0.00
84/04/25	12	16823.00	1180.00	648.50	134.50	86.00	28.55	2.80
84/04/25	15	32965.50	1535.00	293.00	80.00	57.50	39.05	0.00
84/04/25	16	18523.00	380.00	273.00	85.00	34.00	33.85	0.30
84/04/25	21	26210.50	755.00	337.50	109.50	89.50	16.00	4.30
84/05/23	1	24344.00	1990.00	735.00	243.50	57.50	65.00	5.00
84/05/23	2	24156.50	1845.00	592.50	171.00	49.00	40.00	1.60
84/05/23	4	22294.00	1340.00	512.50	154.50	70.00	40.00	2.45
84/05/23	5	27456.50	2835.00	595.50	192.00	52.00	50.00	4.15
84/05/23	7	14519.00	475.00	462.00	121.50	28.00	15.00	2.05
84/05/23	8	11369.00	375.00	327.00	42.00	20.50	25.00	4.95
84/05/23	9	20756.50	1380.00	365.00	239.00	46.50	60.00	4.75
84/05/23	12	23269.00	1345.00	597.50	118.50	87.00	40.00	3.55
84/05/23	15	26381.50	1680.00	515.50	133.00	61.50	75.00	3.50
84/05/23	16	20931.50	340.00	297.50	77.50	39.00	35.00	4.50
84/05/23	21	20594.00	775.00	452.00	113.00	96.00	30.00	2.35
84/06/20	1	20509.50	1610.00	574.00	105.50	45.00	41.70	1.75
84/06/20	2	25397.00	1970.00	1244.00	201.00	70.00	69.65	1.95
84/06/20	4	13809.50	595.00	392.00	81.50	30.50	18.05	1.20
84/06/20	5	24459.50	3265.00	541.50	215.50	65.00	61.90	2.95
84/06/20	7	18922.00	1285.00	581.00	190.00	41.00	38.00	4.20
84/06/20	8	16709.50	710.00	497.50	104.00	37.50	30.85	3.95
84/06/20	9	19959.50	1145.00	348.50	118.50	35.50	19.00	2.10
84/06/20	12	18072.00	1790.00	926.50	146.00	91.50	37.00	3.65
84/06/20	15	20884.50	2265.00	525.50	188.00	88.00	54.25	2.85
84/06/20	16	22195.00	640.00	466.50	85.00	48.50	14.45	6.60
84/06/20	21	23959.50	1455.00	644.00	183.50	135.50	49.85	4.30
84/07/18	1	18782.00	1145.00	486.00	141.50	49.50	28.00	3.45
84/07/18	2	30899.50	2030.00	602.50	182.00	69.50	49.45	4.10
84/07/18	4	30224.50	1515.00	589.50	159.50	57.50	55.75	2.30
84/07/18	5	26999.50	2145.00	487.50	137.50	57.00	67.55	2.25
84/07/18	7	20912.00	1110.00	497.00	189.00	49.50	42.25	3.85
84/07/18	8	15799.50	815.00	457.00	100.00	33.50	63.00	3.30
84/07/18	9	16262.00	655.00	254.50	80.50	35.50	15.20	2.75
84/07/18	12	22349.50	2200.00	817.50	153.50	78.00	45.60	4.20
84/07/18	15	42194.50	2920.00	553.50	257.50	99.50	61.20	3.30
84/07/18	16	19637.00	475.00	392.00	110.50	51.00	30.05	4.45
84/07/18	21	23387.00	1255.00	587.50	102.00	136.00	33.15	2.40

Topsoil Data (mg/kg)

Date	Location	Iron	Lead	Zinc	Copper	Chromium	Nickel	Cadmium
83/08/01	ta	11465.00	28.50	30.00	16.55	23.85	10.40	0.38
83/10/05	ta	7469.50	18.50	66.00	19.50	23.50	6.50	0.85
83/08/01	tb	17820.00	27.50	75.00	31.95	25.40	20.10	0.23
83/10/05	tb	16632.00	93.00	225.50	54.00	40.50	24.55	0.00
83/08/01	tc	19450.00	14.00	40.00	24.05	33.15	19.30	0.10
83/10/05	tc	20204.50	25.00	127.50	37.00	52.00	31.80	0.25
83/08/01	td	19260.00	34.00	60.00	24.85	32.50	20.90	0.42
83/10/05	td	17909.50	57.00	121.50	31.60	52.50	21.05	0.00
83/08/01	te	14585.00	22.50	30.00	18.70	26.15	14.45	0.24
83/10/05	te	12764.50	32.00	80.50	21.00	25.50	9.45	0.90
83/08/01	tf	19865.00	182.00	1080.00	574.80	60.00	42.35	3.19
83/10/05	tf	20667.00	173.00	1124.50	581.00	56.50	36.00	3.00
83/08/01	tg	11870.00	22.50	35.00	15.20	22.45	11.15	0.41
83/10/05	tg	15107.00	53.50	126.50	26.50	179.50	5.35	1.80
83/08/01	th	16835.00	32.50	45.00	37.70	28.90	14.65	0.19
83/10/05	th	14594.50	67.00	239.50	49.50	33.00	18.85	0.20
83/08/01	ti	18560.00	93.00	710.00	70.20	25.80	31.90	0.88
83/10/05	ti	21667.00	161.50	752.00	330.00	29.00	27.75	0.00
83/08/01	tj	12200.00	99.50	180.00	57.45	39.85	20.65	1.34
83/10/05	tj	15619.50	61.50	178.50	37.00	37.00	24.55	1.35

Subsoil Data (mg/kg)

Date	Location	Iron	Lead	Zinc	Copper	Chromium	Nickel	Cadmium
83/08/01	sa	15895.00	27.50	65.00	18.25	28.25	15.50	0.19
83/10/05	sa	13314.50	41.00	89.00	23.50	35.50	19.05	0.60
83/08/01	sb	16535.00	18.50	40.00	27.00	23.80	18.90	0.32
83/10/05	sb	17884.50	91.00	229.50	174.50	39.50	23.35	0.00
83/08/01	sc	22650.00	14.00	60.00	27.10	37.30	22.15	0.17
83/10/05	sc	20217.00	22.50	197.00	35.00	39.00	19.60	0.00
83/08/01	sd	16490.00	26.50	40.00	23.10	29.80	19.35	0.31
83/10/05	sd	16429.50	26.00	103.50	27.00	34.50	17.65	0.00
83/08/01	se	26115.00	3.50	25.00	15.80	17.40	3.75	0.13
83/10/05	se	14009.50	11.50	63.00	15.50	17.50	9.05	1.90
83/08/01	sf	13620.00	31.00	40.00	19.55	24.65	13.10	0.25
83/10/05	sf	21304.50	190.00	1092.00	613.00	64.50	44.40	1.35
83/08/01	sg	12400.00	26.00	30.00	15.60	22.40	10.85	0.24
83/10/05	sg	11069.50	70.00	141.50	32.00	60.00	8.75	0.00
83/08/01	sh	14850.00	29.50	35.00	39.10	29.20	14.50	0.33
83/10/05	sh	17657.00	41.50	114.00	44.00	29.50	12.95	0.00
83/08/01	si	11390.00	59.50	195.00	41.40	20.65	15.25	0.40
83/10/05	si	12627.00	66.00	223.00	46.00	22.00	14.00	0.85
83/08/01	sj	13485.00	54.00	160.00	34.50	37.98	16.25	0.91
83/10/05	sj	14824.50	63.00	168.00	33.00	33.00	15.55	0.00

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Particulate Stormwater Data (mg/l)

Date	Time	Flow	Iron	Lead	Zinc	Copper	Chromium	Nickel	Cadmium
83/08/16	0	0.00	0.006500000	0.001000000	0.003000000	0.001000000	0.002500000	0.015000000	0.000750000
83/08/16	2305	155.00	2.365000000	0.019000000	0.033000000	0.022000000	0.006500000	0.000000000	0.000200000
83/08/16	2308	163.91	2.668500000	0.039000000	0.062500000	0.032500000	0.020500000	0.000000000	0.000000000
83/08/16	2312	212.50	6.016500000	0.080500000	0.092500000	0.050000000	0.021000000	0.005000000	0.000200000
83/08/16	2315	206.25	6.118500000	0.103500000	0.107500000	0.054000000	0.034000000	0.014500000	0.000000000
83/08/16	2318	200.00	3.843500000	0.093000000	0.076000000	0.042000000	0.023500000	0.010500000	0.000000000
83/08/16	2321	191.25	4.343500000	0.086500000	0.078500000	0.042500000	0.025500000	0.000000000	0.000000000
83/08/16	2324	163.91	3.119000000	0.041000000	0.042500000	0.023500000	0.022000000	0.000000000	0.000000000
83/08/16	2328	145.63	4.193500000	0.039500000	0.037000000	0.024000000	0.035000000	0.000000000	0.001450000
83/08/16	2331	130.63	2.901000000	0.036000000	0.034000000	0.024500001	0.013000000	0.000000000	0.000000000
83/08/16	2334	115.00	2.449500000	0.022500000	0.025500000	0.016500000	0.014500000	0.000000000	0.000000000
83/08/16	2337	105.00	2.255000000	0.018500000	0.024500000	0.013000000	0.017000000	0.000000000	0.000000000
83/08/16	2340	95.00	2.155500000	0.025500000	0.022000000	0.012000000	0.021500000	0.002500000	0.000450000
83/08/16	2344	85.00	1.576000000	0.020000000	0.016000000	0.011000000	0.006500000	0.000000000	0.000150000
83/08/16	2347	85.00	1.097500000	0.006500000	0.009500000	0.005000000	0.008000000	0.000000000	0.000000000
83/08/16	2350	85.00	1.274000000	0.014000000	0.011000000	0.006500000	0.008000000	0.000000000	0.000000000
83/09/16	0	0.00	0.100000000	0.003240000	0.006010000	0.002310000	0.001380000	0.000324000	0.000000000
83/09/16	1546	90.00	4.821400000	0.081860000	0.093490000	0.019190000	0.013820000	0.011376000	0.000413200
83/09/16	1550	250.00	6.367500000	0.122160000	0.133290000	0.031890000	0.019420000	0.015576000	0.000925900
83/09/16	1554	586.25	6.813200000	0.109960000	0.120790000	0.029490000	0.020020000	0.014776000	0.000826400
83/09/16	1557	333.59	4.638000000	0.058860000	0.086890000	0.018190000	0.018220000	0.009776000	0.001869000
83/09/16	1600	296.09	5.433000000	0.074060000	0.092490000	0.018390000	0.023620000	0.011276000	0.000000000
83/09/16	1603	250.00	3.763000000	0.066760000	0.072090000	0.014490000	0.015420000	0.007176000	0.000000000
83/09/16	1608	191.25	2.202000000	0.034460000	0.046290000	0.008390000	0.009720000	0.004906000	0.000396800
83/09/16	1611	187.81	1.612700000	0.021260000	0.031690000	0.005870000	0.005890000	0.005126000	0.000909000
83/09/16	1614	163.91	1.111500000	0.012960000	0.024490000	0.004170000	0.005100000	0.007976000	0.000000000
83/09/16	1617	140.00	1.314500000	0.016760000	0.028490000	0.005410000	0.006340000	0.007676000	0.000000000
83/09/16	1621	115.00	1.250000000	0.009460000	0.025350000	0.004050000	0.003160000	0.002946000	0.000000000
83/09/16	1624	90.00	1.340900000	0.011760000	0.027590000	0.004960000	0.011320000	0.002536000	0.000454500
83/10/10	0	0.00	0.047810000	0.000000000	0.002193000	0.001316000	0.000438590	0.000000000	0.000000000
83/10/10	512	140.00	0.955790000	0.014800000	0.008207000	0.002684000	0.003561410	0.000000000	0.001080000
83/10/10	518	105.00	1.463890000	0.022500000	0.013007000	0.004566000	0.007861410	0.000000000	0.000049020
83/10/10	524	90.00	0.945990000	0.015700000	0.007807000	0.002970000	0.011941410	0.000000000	0.000904800
83/10/10	530	125.47	0.602190000	0.004245000	0.005354000	0.001985800	0.009471410	0.000000000	0.001085000
83/10/10	537	95.00	0.534690000	0.011470000	0.004688000	0.001895000	0.003230410	0.004082000	0.001697000
83/10/10	543	77.34	0.502590000	0.005646000	0.009737000	0.002812000	0.001854410	0.004449000	0.001147000
83/10/10	549	74.84	0.459090000	0.002907000	0.003621000	0.001591000	0.003049410	0.005697000	0.000000000
83/10/10	614	250.00	0.210890000	0.000396820	0.001378000	0.000668000	0.003132410	0.000000000	0.000000000
83/10/10	620	324.80	0.449390000	0.005092000	0.004288000	0.001461000	0.003727410	0.000000000	0.000324670
83/10/10	627	365.82	0.670240000	0.003241000	0.005677000	0.001461000	0.004653410	0.000000000	0.000925920
83/10/10	633	315.63	0.861290000	0.012270000	0.007152000	0.002320000	0.004106410	0.000000000	0.000681820
83/10/10	639	250.00	0.962590000	0.013640000	0.007352000	0.002775000	0.005924410	0.000000000	0.000500000
83/10/10	646	191.25	0.792190000	0.013640000	0.007352000	0.002775000	0.003197410	0.000000000	0.000772730
83/10/10	652	195.31	0.543090000	0.010000000	0.004170000	0.001411000	0.005015410	0.000000000	0.001136000
83/10/10	658	243.75	0.441290000	0.009091000	0.003261000	0.001411000	0.001834410	0.003773000	0.000000000
83/10/10	704	265.74	0.463590000	0.006364000	0.003716000	0.000957000	0.003652410	0.000000000	0.001000000
83/10/10	711	493.75	0.575390000	0.006364000	0.004625000	0.001866000	0.001834410	0.003500000	0.000000000
83/10/10	717	531.25	0.748090000	0.012730000	0.005534000	0.001411000	0.003652410	0.000000000	0.000000000
83/10/10	723	446.88	0.694290000	0.006144000	0.006579000	0.001754000	0.003069410	0.002149000	0.000482450
83/10/10	730	400.00	0.563090000	0.007895000	0.004385000	0.001315000	0.001315410	0.000000000	0.001272000
83/10/10	736	333.59	0.519690000	0.008333000	0.003070000	0.000877000	0.003946410	0.000000000	0.008772000
83/10/10	742	275.00	0.479790000	0.003070000	0.003509000	0.000877000	0.003946410	0.000000000	0.000000000
83/10/10	749	218.75	0.433290000	0.004386000	0.002632000	0.000877000	0.003508410	0.001140000	0.000921052

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Particulate Stormwater Data (mg/l)

Date	Time	Flow	Iron	Lead	Zinc	Copper	Chromium	Nickel	Cadmium
83/10/10	755	187.81	0.310090000	0.001315700	0.001754000	0.000438000	0.002631410	0.000000000	0.000000000
83/10/10	801	163.91	0.375390000	0.006364000	0.002807000	0.000957000	0.003197410	0.000000000	0.000000000
83/11/02	0	0.00	0.002550000	0.000000000	0.000000000	0.002000000	0.004000000	0.000000000	0.000000000
83/11/02	1730	493.75	11.447450000	0.317000000	0.006000000	0.126500000	0.033500000	0.011050000	0.002050000
83/11/02	1733	400.00	12.897450000	0.276500000	0.006500000	0.102000000	0.054500000	0.034800000	0.001550000
83/11/02	1736	333.59	13.897450000	0.320500000	0.009500000	0.106500000	0.036000000	0.028000000	0.001700000
83/11/02	1739	218.75	13.447450000	0.257000000	0.008500000	0.089500000	0.037000000	0.018450000	0.001300000
83/11/02	1743	250.00	0.000000000	0.000000000	0.000000000	0.000000000	0.000000000	0.000000000	0.000000000
83/11/02	1746	285.74	12.347450000	0.203500000	0.006500000	0.084500000	0.036000000	0.016350000	0.001100000
83/11/02	1753	191.25	29.447450000	0.413000000	0.033000000	0.150000000	0.064500000	0.040650000	0.001750000
83/11/02	1758	163.91	15.297450000	0.082500000	0.003500000	0.035000000	0.021500000	0.033750000	0.000750000
83/11/02	1800	140.00	2.207450000	0.023500000	0.006500000	0.006500000	0.020000000	0.015800000	0.001250000
83/11/02	1807	90.00	1.454450000	0.017500000	0.000500000	0.005000000	0.009000000	0.018550000	0.000950000
83/11/03	0	0.00	0.002550000	0.000000000	0.000000000	0.002000000	0.004000000	0.000000000	0.000000000
83/11/03	20	218.75	1.018950000	0.004000000	0.000500000	0.002000000	0.018000000	0.017750000	0.000550000
83/11/03	26	191.25	0.938950000	0.006000000	0.000500000	0.002000000	0.040500000	0.016600000	0.000000000
83/11/03	32	200.00	2.341950000	0.020000000	0.001000000	0.007500000	0.012500000	0.010900000	0.000250000
83/11/03	39	206.25	1.867450000	0.011500000	0.000500000	0.006000000	0.008000000	0.005250000	0.000350000
83/11/03	45	163.91	1.224450000	0.014500000	0.000500000	0.003500000	0.009000000	0.010550000	0.000000000
83/11/03	51	140.00	0.970450000	0.008500000	0.000500000	0.001500000	0.009000000	0.000000000	0.000450000
83/11/03	58	130.63	0.591450000	0.009500000	0.000500000	0.001500000	0.003500000	0.011950000	0.000750000
83/11/03	107	110.00	0.537950000	0.004500000	0.000000000	0.000000000	0.003500000	0.006600000	0.000150000
83/11/03	110	95.00	0.193450000	0.007500000	0.000000000	0.000000000	0.002000000	0.002550000	0.000650000
83/11/03	212	95.00	0.146950000	0.003500000	0.000000000	0.000000000	0.000000000	0.001150000	0.000950000
83/11/03	216	90.00	0.152950000	0.009000000	0.000000000	0.000000000	0.000000000	0.001250000	0.000850000
83/11/25	0	0.00	0.005217400	0.001739000	0.004782600	0.000608690	0.001869000	0.007826000	0.000000000
83/11/25	1521	135.47	1.518782600	0.028261000	0.020417400	0.013191310	0.016131000	0.000000000	0.000000000
83/11/25	1524	140.00	1.126782600	0.025261000	0.013917400	0.009891310	0.010131000	0.000000000	0.000217390
83/11/25	1527	142.34	1.130782600	0.021261000	0.011717400	0.007739110	0.009131000	0.000000000	0.000000000
83/11/25	1530	145.63	0.914282600	0.024261000	0.009517400	0.006782610	0.009831000	0.000000000	0.000000000
83/11/25	1536	142.34	1.070382600	0.014261000	0.007817400	0.005260810	0.012531000	0.000000000	0.000000000
83/11/25	1543	145.63	0.736782600	0.005217000	0.004782400	0.004956510	0.015531000	0.002174000	0.000434780
83/11/25	1549	142.34	0.579482600	0.009961000	0.003912400	0.002869510	0.008431000	0.005674000	0.000304350
83/11/25	1555	140.00	0.637382600	0.012161000	0.003912400	0.002652110	0.011631000	0.000000000	0.000086956
83/11/25	1602	135.47	0.308682600	0.017861000	0.006017400	0.003956510	0.009831000	0.000000000	0.000347820
83/11/25	1608	130.63	0.793382600	0.004782000	0.006517400	0.003304310	0.011131000	0.000000000	0.000000000
83/11/25	1614	120.00	2.319482600	0.055261000	0.034717400	0.025291310	0.017131000	0.000000000	0.000130430
83/11/25	1620	110.00	2.344282600	0.092261000	0.046017400	0.050561310	0.023731000	0.000000000	0.000347820
83/11/25	1627	90.00	2.344782600	0.134261000	0.049517400	0.063491310	0.019731000	0.000000000	0.000478260
83/11/25	1651	95.00	2.401782600	0.219261000	0.055617400	0.083691310	0.030431000	0.000000000	0.000391300
83/11/25	1658	100.00	2.272782600	0.104261000	0.045617400	0.058391310	0.023131000	0.000000000	0.000347820
83/11/25	1704	95.00	1.750782600	0.054261000	0.028717400	0.040791310	0.014231000	0.016474000	0.000086956
83/11/25	1710	120.00	1.353782600	0.037261000	0.021717400	0.022791310	0.015531000	0.000435000	0.000086956
83/11/25	1717	191.25	1.380782600	0.028261000	0.016017400	0.010091310	0.009331000	0.000000000	0.000260870
83/11/25	1723	195.31	0.726782600	0.009261000	0.007817400	0.004477310	0.005827000	0.000000000	0.000043478
83/11/25	1729	250.00	1.202582600	0.013261000	0.015617400	0.007174310	0.005478000	0.000000000	0.000217390
83/11/25	1736	400.00	1.495182600	0.027261000	0.022617400	0.012991310	0.009231000	0.000000000	0.000043478
83/11/25	1742	400.00	1.856482600	0.036261000	0.033817400	0.022691310	0.013731000	0.009574000	0.000260870
83/11/25	1748	446.88	1.676982600	0.027261000	0.025617400	0.014191310	0.009131000	0.000000000	0.000086956
83/11/25	1754	400.00	1.489982600	0.023261000	0.021717400	0.011691310	0.008731000	0.000000000	0.000304350
83/11/25	1801	350.00	1.458682600	0.017261000	0.023517400	0.012191310	0.007435000	0.000000000	0.000434780
83/11/25	1807	250.00	1.658782600	0.016261000	0.019117400	0.008695310	0.005131000	0.000000000	0.000043478
83/12/17	0	0.00	0.030000000	0.000000000	0.005000000	0.001875000	0.001250000	0.005000000	0.000000000

Particulate Stormwater Data (mg/l)

Date	Time	Flow	Iron	Lead	Zinc	Copper	Chromium	Nickel	Cadmium
83/12/17	454	90.00	0.547000000	0.000625000	0.003750000	0.000625000	0.001875000	0.000000000	0.001125000
83/12/17	457	90.00	0.489000000	0.000000000	0.004370000	0.001875000	0.002500000	0.000000000	0.002940000
83/12/17	501	85.00	0.501000000	0.000000000	0.003750000	0.001250000	0.001875000	0.000000000	0.002440000
83/12/17	504	80.00	0.414000000	0.002500000	0.002500000	0.001250000	0.002500000	0.000000000	0.000000000
83/12/17	507	77.34	0.334000000	0.000000000	0.001870000	0.001250000	0.004370000	0.000000000	0.002440000
83/12/17	510	75.63	0.493000000	0.000625000	0.004370000	0.001250000	0.005000000	0.000000000	0.001250000
83/12/17	513	74.84	0.225000000	0.001250000	0.000000000	0.000625000	0.000000000	0.000000000	0.000000000
83/12/17	1101	255.47	1.428000000	0.038100000	0.017500000	0.005625000	0.003750000	0.000000000	0.000562000
83/12/17	1104	333.59	2.226000000	0.029400000	0.030000000	0.007495000	0.008120000	0.000000000	0.000562000
83/12/17	1107	378.32	2.602000000	0.025000000	0.040000000	0.009375000	0.015550000	0.000000000	0.000197000
83/12/17	1110	385.16	2.923000000	0.038100000	0.033100000	0.006875000	0.014350000	0.003750000	0.000000000
83/12/17	1113	385.16	3.562000000	0.039400000	0.040600000	0.009375000	0.017450000	0.001250000	0.000000000
83/12/17	1117	371.88	2.727000000	0.040000000	0.028700000	0.006250000	0.011250000	0.000000000	0.000000000
83/12/17	1120	354.88	2.682000000	0.028700000	0.031200000	0.007495000	0.010000000	0.000000000	0.000250000
84/01/02	0	0.00	0.000000000	0.000000000	0.000000000	0.000000000	0.000000000	0.000000000	0.000000000
84/01/02	1324	105.00	0.342000000	0.009610000	0.006730000	0.003850000	0.010600000	0.008650000	0.000481000
84/01/02	1330	110.00	0.129000000	0.018300000	0.005770000	0.002880000	0.001920000	0.043000000	0.000000000
84/01/02	1336	115.00	0.169000000	0.000000000	0.006730000	0.003850000	0.003850000	0.011500000	0.000000000
84/01/02	1343	110.00	0.118000000	0.006730000	0.007690000	0.002880000	0.003850000	0.000000000	0.000961000
84/01/02	1349	100.00	0.214000000	0.014400000	0.005770000	0.001920000	0.009620000	0.006730000	0.003270000
84/01/02	1355	120.00	0.152000000	0.000962000	0.004810000	0.001920000	0.005770000	0.000000000	0.000000000
84/01/02	1401	130.63	0.186000000	0.000000000	0.004810000	0.004810000	0.000000000	0.000000000	0.000000000
84/01/02	1408	140.00	0.170000000	0.024000000	0.006730000	0.003850000	0.000962000	0.000000000	0.001060000
84/01/02	1414	149.84	0.237000000	0.007690000	0.006730000	0.002880000	0.000000000	0.000000000	0.000192000
84/01/02	1420	191.25	0.235000000	0.009610000	0.004810000	0.001920000	0.001920000	0.000000000	0.002590000
84/01/02	1426	218.75	0.222000000	0.000000000	0.004810000	0.001920000	0.000000000	0.000000000	0.002310000
84/01/02	1433	231.25	0.242000000	0.005770000	0.004810000	0.002880000	0.000000000	0.000000000	0.003750000
84/01/02	1439	243.75	0.307000000	0.000000000	0.004810000	0.001920000	0.000000000	0.000000000	0.003460000
84/01/02	1445	250.00	0.290000000	0.000000000	0.006730000	0.001920000	0.001920000	0.001920000	0.000000000
84/01/02	1452	255.47	0.251000000	0.000000000	0.005770000	0.001920000	0.000000000	0.000962000	0.001640000
84/01/02	1458	261.46	0.261000000	0.004810000	0.006730000	0.002880000	0.006710000	0.000000000	0.000000000
84/01/02	1504	261.46	0.154000000	0.000000000	0.005770000	0.000962000	0.010600000	0.006710000	0.003460000
84/01/02	1510	237.50	0.257000000	0.004810000	0.004810000	0.000962000	0.009620000	0.000000000	0.001060000
84/01/02	1517	206.25	0.228000000	0.000000000	0.006730000	0.001920000	0.004810000	0.000000000	0.004900000
84/01/02	1523	191.25	0.224000000	0.000000000	0.005770000	0.000962000	0.011500000	0.009620000	0.001150000
84/01/02	1529	187.81	0.222000000	0.002880000	0.005770000	0.001920000	0.007690000	0.000000000	0.003560000
84/01/02	1535	191.25	0.207000000	0.002880000	0.005770000	0.001920000	0.004810000	0.000000000	0.000000000
84/01/02	1542	225.00	0.252000000	0.000000000	0.004810000	0.001920000	0.001920000	0.000000000	0.001630000
84/01/02	1548	250.00	0.246000000	0.003850000	0.004810000	0.001920000	0.005770000	0.000000000	0.000000000
84/01/22	0	0.00	0.026000000	0.000000000	0.001000000	0.002000000	0.005000000	0.004300000	0.000000000
84/01/22	1259	90.00	2.737000000	0.018300000	0.036200000	0.005930000	0.013290000	0.001553600	0.000000000
84/01/22	1305	90.00	2.423000000	0.022600000	0.035200000	0.005071000	0.011660000	0.001138590	0.000514035
84/01/22	1311	95.00	3.852000000	0.038460000	0.054130000	0.010820000	0.020641000	0.005315380	0.000000000
84/01/22	1318	100.00	2.632000000	0.036720000	0.035720000	0.004250000	0.015312000	0.004293750	0.000000000
84/01/22	1324	102.50	2.495000000	0.007895000	0.033200000	0.004140000	0.014298000	0.010170000	0.001578940
84/01/22	1330	105.00	2.751500000	0.020000000	0.030250000	0.004250000	0.008125000	0.000000000	0.000000000
84/01/22	1336	110.00	2.313500000	0.025000000	0.031250000	0.005258000	0.004677410	0.005216120	0.000000000
84/01/22	1342	110.00	1.755400000	0.026200000	0.024640000	0.005051000	0.006538400	0.000829200	0.000000000
84/01/22	1348	120.00	2.080000000	0.040510000	0.027440000	0.009344000	0.013103400	0.000000000	0.000000000
84/01/22	1355	120.00	2.122300000	0.026660000	0.028160000	0.005500000	0.010833000	0.006033000	0.000416666
84/01/22	1401	130.63	2.120910000	0.013920000	0.026320000	0.004185000	0.006855600	0.012452500	0.000412371
84/01/22	1407	135.47	1.817100000	0.017650000	0.023500000	0.002411700	0.003823520	0.000000000	0.000784313
84/01/22	1413	135.47	2.115660000	0.017500000	0.028760000	0.005141800	0.002738090	0.000000000	0.001190470

Particulate Stormwater Data (mg/l)

Date	Time	Flow	Iron	Lead	Zinc	Copper	Chromium	Nickel	Cadmium
84/01/22	1419	135.47	1.728440000	0.026660000	0.022330000	0.002444000	0.003333330	0.000000000	0.001000000
84/01/22	1426	140.00	3.211500000	0.033920000	0.043640000	0.006035700	0.014642800	0.004717850	0.000000000
84/01/22	1432	140.00	1.693900000	0.020370000	0.020290000	0.002166600	0.003333330	0.000000000	0.000000000
84/01/22	1438	140.00	1.990490000	0.017520000	0.023740000	0.003154600	0.002731950	0.000000000	0.000000000
84/01/22	1444	140.00	1.428800000	0.017740000	0.018890000	0.002301070	0.001989240	0.009678400	0.001182790
84/01/22	1450	135.47	1.324000000	0.019230000	0.017130000	0.002945050	0.002692300	0.003721970	0.001263730
84/01/22	1457	135.47	1.296200000	0.013425000	0.016130000	0.001240740	0.003333330	0.007737000	0.001296290
84/01/22	1503	135.47	1.104690000	0.001123500	0.015850000	0.002494000	0.006797700	0.007722400	0.000000000
84/01/22	1509	130.63	1.173020000	0.008823500	0.013705000	0.000450900	0.004803920	0.003494110	0.001372540
84/01/22	1515	130.63	1.107800000	0.009677400	0.019160000	0.005258100	0.004677410	0.000749010	0.000441176
84/01/22	1521	120.00	0.940400000	0.021093000	0.013840000	0.000347500	0.002031250	0.004137500	0.000234375
84/05/10	0	0.00	0.012096700	0.004032250	0.001612900	0.000000000	0.003629000	0.000000000	0.000000000
84/05/10	1733	0.00	22.860887300	0.766128750	0.506452100	0.296271000	0.127419000	0.088709600	0.005927410
84/05/10	1737	0.00	14.756048300	0.427419750	0.363710100	0.164919000	0.060887000	0.040322500	0.008065410
84/05/10	1742	0.00	11.893064300	0.278225750	0.286693100	0.112903000	0.081452000	0.032258000	0.003024190
84/05/10	1746	0.00	11.681451300	0.209677350	0.188710100	0.088306000	0.040323000	0.012096700	0.002137090
84/05/10	1750	0.00	11.477822300	0.294354850	0.269003100	0.165323000	0.052823000	0.032258000	0.003991930
84/05/10	1754	0.00	19.554435300	0.637096750	0.489919100	0.275403000	0.079436000	0.064516100	0.003508060
84/05/10	1758	0.00	15.663306300	0.491935450	0.320161100	0.166532000	0.062500000	0.040322500	0.003306450
84/05/10	1802	0.00	12.558468300	0.205645150	0.178629100	0.084677000	0.045160000	0.024193500	0.000645161
84/05/10	1806	0.00	11.189516300	0.237903150	0.136290100	0.072581000	0.029435500	0.016129000	0.001290320
84/05/10	1810	0.00	7.584677500	0.112903150	0.088709100	0.035709600	0.032258000	0.012096700	0.000685483
84/05/10	1814	0.00	5.840725900	0.060483850	0.079032100	0.036694000	0.033064500	0.008064510	0.000685483
84/05/10	1818	0.00	4.788306500	0.048387050	0.066129100	0.037097000	0.029435500	0.000000000	0.000443548
84/05/10	1822	0.00	4.258064600	0.040322750	0.062096100	0.035484000	0.011693500	0.000000000	0.000322580
84/05/10	1826	0.00	3.786290400	0.032257750	0.053226100	0.031048000	0.022532200	0.016129000	0.000282258
84/05/10	1830	0.00	2.885080700	0.020161750	0.041129100	0.018952000	0.011693500	0.020161200	0.000201612
84/05/10	1834	0.00	1.631048500	0.008064750	0.032258100	0.014112900	0.008871000	0.004032250	0.000241935
84/05/10	1838	0.00	1.834677500	0.004032250	0.027822100	0.011693500	0.008064500	0.004032250	0.000483870
84/05/10	1842	0.00	1.290322700	0.000000000	0.016935100	0.006854800	0.011693500	0.008064510	0.000080645
84/05/10	1846	0.00	1.560483900	0.016128950	0.019758100	0.007661300	0.010887100	0.000000000	0.000120967
84/05/10	1848	0.00	1.788306500	0.020161250	0.018548300	0.006451600	0.031451600	0.008064510	0.000362903
84/05/24	0	0.00	0.000000000	0.008064510	0.002419350	0.000806451	0.001209670	0.000000000	0.000282258
84/05/24	1540	2012.54	14.556452000	0.673387090	0.289516050	0.214516049	0.072580630	0.051209600	0.004838702
84/05/24	1548	1550.00	10.221774000	0.262096690	0.207661250	0.090322549	0.050806430	0.032661200	0.002943542
84/05/24	1556	1300.00	8.497903200	0.241935490	0.197580650	0.079435449	0.039516130	0.026209600	0.002056442
84/05/24	1605	586.25	6.945564500	0.278225790	0.185887050	0.082661249	0.034274130	0.017338700	0.002177412
84/05/24	1613	400.00	3.895161300	0.040322490	0.051209650	0.013709649	0.011290330	0.016129000	0.000403225
84/05/24	1621	191.25	3.411935500	0.016128990	0.042741850	0.013709649	0.008467740	0.013306400	0.000000000
84/05/24	1629	110.00	3.074596800	0.012096690	0.034677350	0.010483849	0.009274130	0.016935400	0.000604838
84/05/24	1638	446.88	2.332661300	0.016128990	0.031854750	0.008064509	0.006451620	0.006854830	0.000120967
84/05/24	1646	365.82	3.798387100	0.024193490	0.046370950	0.011290249	0.010887030	0.015725800	0.000443548
84/05/24	1654	250.00	2.441532300	0.016128990	0.031451550	0.008064509	0.006451620	0.010483800	0.000000000
84/05/24	1703	163.91	3.594758100	0.040322490	0.052419350	0.016128949	0.011290330	0.009677410	0.000000000
84/05/24	1711	110.00	2.203629000	0.008064490	0.027016050	0.007661289	0.006451620	0.000000000	0.001370962
84/05/25	0	0.00	0.000000000	0.008064510	0.002419350	0.000806451	0.001209670	0.000000000	0.000282258
84/05/25	2233	120.00	0.543145100	0.004032190	0.004838710	0.002016129	0.001209680	0.000000000	0.000483871
84/05/25	2237	125.47	0.514112900	0.000000000	0.005241940	0.002419349	0.001612910	0.006451610	0.000483871
84/05/25	2245	135.47	0.560483800	0.000000000	0.005241940	0.002419349	0.000000000	0.002419350	0.000725802
84/05/25	2253	140.00	0.533870900	0.000000000	0.004838710	0.001612899	0.000403230	0.002016120	0.001129032
84/05/25	2301	142.34	0.645161200	0.000000000	0.005241940	0.002419349	0.000806450	0.000000000	0.000806442
84/05/25	2309	191.25	0.548387100	0.000000000	0.004435480	0.001612899	0.002822580	0.000000000	0.000483871
84/05/25	2317	261.46	0.468951600	0.000000000	0.005645160	0.001612899	0.001612910	0.000000000	0.000403225

Particulate Stormwater Data (mg/l)

Date	Time	Flow	Iron	Lead	Zinc	Copper	Chromium	Nickel	Cadmium
84/05/25	2325	250.00	0.310887100	0.000000000	0.003629030	0.001209669	0.000806450	0.002016120	0.001088702
84/05/25	2334	206.25	0.306451600	0.000000000	0.002822580	0.002016129	0.000403230	0.003225800	0.000000000
84/05/25	2342	155.00	0.376161200	0.000000000	0.007258060	0.001209669	0.000806450	0.000000000	0.000362903
84/05/25	2350	120.00	0.329838700	0.000000000	0.004032260	0.001209669	0.000403230	0.002822580	0.001411282
84/06/20	0	0.00	0.009677410	0.000000000	0.001209670	0.000080645	0.000806451	0.003185480	0.000967741
84/06/20	50	90.00	8.137499990	0.189516100	0.141532230	0.072499955	0.031451549	0.021370920	0.000000000
84/06/20	54	195.31	6.566935490	0.169354800	0.166129030	0.067258055	0.022983849	0.013104820	0.000000000
84/06/20	1612	140.00	1.533467790	0.016129000	0.019758030	0.012419355	0.012903149	0.003266130	0.000000000
84/06/20	1617	77.34	4.026612890	0.044354800	0.077822530	0.035806355	0.034274149	0.014637020	0.000443549
84/06/20	1621	120.00	4.710080690	0.048387000	0.064516130	0.047096755	0.044354749	0.008870920	0.006935479
84/06/20	1628	90.00	4.298790290	0.048387000	0.051612830	0.031774155	0.016532249	0.000000000	0.000000000
84/06/20	1632	74.84	4.718145190	0.080645100	0.058064430	0.043870955	0.036693549	0.004596770	0.000000000
84/06/20	1827	558.83	7.175806490	0.177419300	0.096774130	0.037419355	0.067741849	0.021491920	0.000120959
84/06/20	1831	465.63	8.710080690	0.096774100	0.143951530	0.041451555	0.047580549	0.029112820	0.001693549
84/06/20	1835	365.82	8.766693590	0.137096700	0.130241930	0.044274155	0.032258049	0.018991920	0.001169349
84/06/20	1839	306.05	7.792741990	0.088709600	0.097983830	0.038628955	0.037499949	0.014838620	0.000000000
84/06/20	1843	237.50	6.794758090	0.056451600	0.077419330	0.032177355	0.033467649	0.015524120	0.000000000
84/06/20	1848	171.88	6.585080690	0.056451600	0.073790330	0.028145155	0.033064449	0.024354820	0.000000000
84/06/20	1852	120.00	6.407661290	0.068548300	0.080241930	0.029354755	0.027419349	0.021290320	0.000000000
84/06/20	1855	100.00	4.577016090	0.032258000	0.049999930	0.018467655	0.016532249	0.017217720	0.000000000
84/07/15	0	0.00	0.031854800	0.004032250	0.002016120	0.000806451	0.000403225	0.000080645	0.000564516
84/07/15	1132	200.00	3.169919400	0.165322550	0.087096780	0.037499949	0.014112875	0.009193545	0.000927414
84/07/15	1136	191.25	3.693951700	0.145161250	0.071370880	0.021370949	0.015725775	0.011451555	0.000685484
84/07/15	1140	171.88	2.893549400	0.096774150	0.063306380	0.018548349	0.011693475	0.003749995	0.000000000
84/07/15	1144	187.81	1.912500000	0.064516050	0.042338680	0.010887049	0.008870965	0.009798385	0.000645154
84/07/15	1148	163.91	1.583871000	0.060483850	0.034677380	0.010887049	0.004838705	0.003588705	0.001048384
84/07/15	1152	115.00	2.018145200	0.084677350	0.037096780	0.011693549	0.008467735	0.000000000	0.000201613
84/07/15	1156	90.00	2.125000000	0.064516050	0.037903180	0.011693549	0.007258065	0.013628955	0.000846774

Soluble Stormwater Data (mg/l)

Date	Time	Flow	Iron	Lead	Zinc	Copper	Chromium	Nickel	Cadmium
83/08/15	0	0.00	0.000000000	0.000000000	0.000000000	0.000000000	0.000000000	0.000000000	0.000000000
83/08/16	2305	155.00	4.125000000	0.650000000	0.725000000	0.200000000	0.075000000	1.475000000	0.015000000
83/08/16	2308	163.91	5.725000000	0.950000000	0.975000000	0.200000000	0.025000000	0.675000000	0.000000000
83/08/16	2312	212.50	8.175000000	0.575000000	1.225000000	0.225000000	0.050000000	0.000000000	0.015000000
83/08/16	2315	206.25	9.200000000	1.150000000	1.325000000	0.225000000	0.125000000	1.325000000	0.000000000
83/08/16	2318	200.00	6.825000000	1.125000000	1.350000000	0.200000000	0.025000000	0.775000000	0.000000000
83/08/16	2321	191.25	6.275000000	0.200000000	0.800000000	0.125000000	0.150000000	0.050000000	0.022500000
83/08/16	2324	163.91	5.125000000	0.300000000	0.675000000	0.150000000	0.100000000	0.000000000	0.000000000
83/08/16	2328	145.63	4.675000000	0.200000000	0.675000000	0.150000000	0.000000000	0.725000000	0.000000000
83/08/16	2331	130.63	4.475000000	0.475000000	0.750000000	0.200000000	0.200000000	0.550000000	0.042500000
83/08/16	2334	115.00	4.175000000	0.475000000	0.775000000	0.150000000	0.075000000	0.475000000	0.000000000
83/08/16	2337	105.00	3.975000000	0.425000000	0.625000000	0.125000000	0.125000000	0.000000000	0.012500000
83/08/16	2340	95.00	2.525000000	0.500000000	0.425000000	0.100000000	0.000000000	0.475000000	0.052500000
83/08/16	2344	85.00	1.700000000	0.075000000	0.675000000	0.150000000	0.050000000	0.025000000	0.000000000
83/08/16	2347	85.00	3.050000000	0.200000000	0.425000000	0.125000000	0.000000000	0.300000000	0.000000000
83/08/16	2350	85.00	3.700000000	0.400000000	0.675000000	0.150000000	0.125000000	1.350000000	0.012500000
83/09/16	0	0.00	0.120000000	0.005000000	0.125000000	0.010000000	0.002500000	0.004500000	0.000000000
83/09/16	1546	90.00	0.975000000	0.440000000	0.277500000	0.057500000	0.002500000	0.055500000	0.000000000
83/09/16	1550	250.00	1.097500000	0.245000000	0.310000000	0.060000000	0.007500000	0.057000000	0.001500000
83/09/16	1554	586.25	0.737500000	0.260000000	0.260000000	0.050000000	0.012500000	0.017250000	0.002500000
83/09/16	1557	333.59	0.400000000	0.157000000	0.132500000	0.135000000	0.002500000	0.017500000	0.001250000
83/09/16	1600	296.09	0.587500000	0.167500000	0.125000000	0.045000000	0.000000000	0.036750000	0.002750000
83/09/16	1603	250.00	1.065000000	0.392500000	0.202500000	0.050000000	0.007500000	0.071500000	0.006250000
83/09/16	1608	191.25	0.517500000	0.225000000	0.132500000	0.030000000	0.000000000	0.285750000	0.005000000
83/09/16	1611	187.81	0.425000000	0.152500000	0.065000000	0.022500000	0.007500000	0.032250000	0.000000000
83/09/16	1614	163.91	0.380000000	0.152500000	0.275000000	0.020000000	0.000000000	0.036500000	0.000500000
83/09/16	1617	140.00	0.390000000	0.157500000	0.037500000	0.007500000	0.002500000	0.046500000	0.006500000
83/09/16	1621	115.00	0.405000000	0.135000000	0.080000000	0.017500000	0.020000000	0.113250000	0.007500000
83/09/16	1624	90.00	0.460000000	0.175000000	0.125000000	0.022500000	0.000000000	0.008000000	0.002250000
83/10/10	0	0.00	0.018000000	0.000000000	0.008000000	0.000000000	0.000000000	0.000000000	0.001000000
83/10/10	512	140.00	0.634000000	0.102000000	0.170000000	0.036000000	0.000000000	0.000000000	0.000000000
83/10/10	518	105.00	0.714000000	0.192000000	0.096000000	0.030000000	0.014000000	0.000000000	0.000000000
83/10/10	524	90.00	0.718000000	0.118000000	0.182000000	0.060000000	0.022000000	0.203000000	0.003800000
83/10/10	530	125.47	0.408000000	0.036000000	0.084000000	0.022000000	0.022000000	0.245800000	0.000000000
83/10/10	537	95.00	0.474000000	0.070000000	0.300000000	0.020000000	0.000000000	0.008600000	0.004800000
83/10/10	543	77.34	0.538000000	0.076000000	0.566000000	0.022000000	0.000000000	0.034800000	0.008200000
83/10/10	549	74.84	0.602000000	0.142000000	0.094000000	0.030000000	0.008000000	0.021200000	0.004600000
83/10/10	614	250.00	0.580000000	0.052000000	0.072000000	0.040000000	0.014000000	0.054400000	0.000200000
83/10/10	620	324.80	0.500000000	0.100000000	0.254000000	0.030000000	0.010000000	0.012200000	0.000000000
83/10/10	627	365.62	0.714000000	0.046000000	0.060000000	0.022000000	0.008000000	0.025200000	0.000000000
83/10/10	633	315.63	0.702000000	0.142000000	0.096000000	0.042000000	0.008000000	0.000000000	0.000000000
83/10/10	639	250.00	0.584000000	0.066000000	0.108000000	0.030000000	0.002000000	0.026600000	0.001000000
83/10/10	646	191.25	0.940000000	0.130000000	0.112000000	0.050000000	0.000000000	0.017000000	0.005600000
83/10/10	652	195.31	0.720000000	0.158000000	0.140000000	0.088000000	0.010000000	0.084400000	0.005200000
83/10/10	658	243.75	0.488000000	0.154000000	0.080000000	0.034000000	0.000000000	0.032000000	0.001200000
83/10/10	704	285.74	0.510000000	0.262000000	0.090000000	0.046000000	0.000000000	0.029000000	0.000000000
83/10/10	711	493.75	0.488000000	0.130000000	0.110000000	0.038000000	0.012000000	0.018400000	0.002200000
83/10/10	717	531.25	0.552000000	0.130000000	0.100000000	0.024000000	0.010000000	0.014000000	0.000000000
83/10/10	723	446.88	0.376000000	0.094000000	0.056000000	0.014000000	0.006000000	0.021400000	0.000000000
83/10/10	730	400.00	0.382000000	0.092000000	0.084000000	0.032000000	0.004000000	0.023800000	0.000000000
83/10/10	736	333.59	0.568000000	0.144000000	0.090000000	0.024000000	0.000000000	0.073200000	0.000000000
83/10/10	742	275.00	0.382000000	0.084000000	0.060000000	0.022000000	0.008000000	0.024600000	0.004400000
83/10/10	749	218.75	0.390000000	0.090000000	0.090000000	0.026000000	0.004000000	0.017800000	0.005800000

Soluble Stormwater Data (mg/l)

Date	Time	Flow	Iron	Lead	Zinc	Copper	Chromium	Nickel	Cadmium
83/10/10	755	187.81	0.276000000	0.070000000	0.058000000	0.024000000	0.004000000	0.000000000	0.003400000
83/10/10	801	163.91	0.474000000	0.120000000	0.066000000	0.022000000	0.002000000	0.005200000	0.000000000
83/11/02	0	0.00	0.036000000	0.000000000	0.002000000	0.002000000	0.000000000	0.000000000	0.000000000
83/11/02	1730	493.75	3.348000000	0.448000000	0.018000000	0.136000000	0.094000000	0.719600000	0.000200000
83/11/02	1733	400.00	2.708000000	0.458000000	0.016000000	0.076000000	0.080000000	0.796400000	0.004800000
83/11/02	1736	333.59	3.082000000	0.506000000	0.018000000	0.040000000	0.032000000	0.255800000	0.006000000
83/11/02	1739	218.75	3.232000000	0.526000000	0.020000000	0.042000000	0.036000000	0.377000000	0.000000000
83/11/02	1743	250.00	2.042000000	0.508000000	0.014000000	0.050000000	0.028000000	0.339400000	0.004200000
83/11/02	1746	285.74	3.590000000	0.572000000	0.020000000	0.042000000	0.036000000	0.364000000	0.005800000
83/11/02	1753	191.25	4.026000000	0.838000000	0.032000000	0.064000000	0.020000000	0.202000000	0.007000000
83/11/02	1758	163.91	2.910000000	0.538000000	0.016000000	0.072000000	0.014000000	0.088600000	0.003200000
83/11/02	1800	140.00	1.110000000	0.272000000	0.004000000	0.048000000	0.048000000	0.570200000	0.003600000
83/11/02	1807	90.00	0.864000000	0.264000000	0.004000000	0.046000000	0.026000000	0.314800000	0.001800000
83/11/03	0	0.00	0.036000000	0.000000000	0.002000000	0.002000000	0.000000000	0.000000000	0.000000000
83/11/03	20	218.75	0.754000000	0.112000000	0.002000000	0.028000000	0.108000000	1.394000000	0.000600000
83/11/03	26	191.25	0.746000000	0.114000000	0.002000000	0.184000000	0.156000000	1.506800000	0.002800000
83/11/03	32	200.00	1.328000000	0.270000000	0.006000000	0.050000000	0.026000000	0.218800000	0.002200000
83/11/03	39	206.25	1.126000000	0.240000000	0.004000000	0.036000000	0.012000000	0.101800000	0.000400000
83/11/03	45	163.91	0.706000000	0.138000000	0.002000000	0.028000000	0.020000000	0.270200000	0.000200000
83/11/03	51	140.00	0.544000000	0.110000000	0.002000000	0.044000000	0.026000000	0.289800000	0.000000000
83/11/03	58	130.63	0.442000000	0.062000000	0.000000000	0.024000000	0.024000000	0.130400000	0.000800000
83/11/03	107	110.00	0.434000000	0.052000000	0.000000000	0.022000000	0.012000000	0.130800000	0.000400000
83/11/03	110	95.00	0.182000000	0.050000000	0.004000000	0.024000000	0.014000000	0.020200000	0.000000000
83/11/03	212	95.00	0.210000000	0.066000000	0.000000000	0.016000000	0.008000000	0.056200000	0.000000000
83/11/03	216	90.00	0.160000000	0.026000000	0.000000000	0.016000000	0.008000000	0.089600000	0.000000000
83/11/25	0	0.00	0.000000000	0.000000000	0.003999700	0.000999925	0.000000000	0.000000000	0.000000000
83/11/25	1521	135.47	1.119985000	0.289972500	0.173997300	0.046200100	0.035201500	0.399970000	0.000799825
83/11/25	1524	140.00	0.981985000	0.245985000	0.146000550	0.041199900	0.026398250	0.260015000	0.001400125
83/11/25	1527	142.34	1.531800000	0.360007500	0.180000300	0.057000325	0.023598000	0.283992500	0.001200025
83/11/25	1530	145.63	1.357977500	0.287960000	0.157995050	0.049199875	0.033798500	0.283992500	0.002199950
83/11/25	1536	142.34	0.651992500	0.184000000	0.100000550	0.034799575	0.032596750	0.195960000	0.000400200
83/11/25	1543	145.63	0.433952500	0.161977500	0.077995300	0.027198075	0.029198500	0.241960000	0.002199950
83/11/25	1549	142.34	0.587995000	0.201997500	0.107952800	0.038002325	0.028399250	0.181987500	0.001999850
83/11/25	1555	140.00	0.659985000	0.227987500	0.121982800	0.044200825	0.033597250	0.222007500	0.001999850
83/11/25	1602	135.47	0.843985000	0.237992500	0.129975300	0.040796825	0.026197000	0.186012500	0.001200025
83/11/25	1608	130.63	0.477997500	0.191992500	0.098005300	0.031401325	0.023598000	0.161977500	0.000000000
83/11/25	1614	120.00	2.263775000	0.572010000	0.303970300	0.074399825	0.015795250	0.114022500	0.001400125
83/11/25	1620	110.00	2.496075000	0.449995000	0.315987800	0.046397325	0.026599500	0.270020000	0.001200025
83/11/25	1627	90.00	2.753675000	0.396094500	0.341977800	0.036599325	0.019596000	0.230000000	0.001200025
83/11/25	1651	95.00	3.072225000	0.277955000	0.343990300	0.017595575	0.086192500	0.483977500	0.001799750
83/11/25	1658	100.00	2.731825000	0.406007500	0.303970300	0.035397575	0.041595500	0.314007500	0.001999850
83/11/25	1704	95.00	2.520225000	0.373980000	0.279992800	0.036996075	0.032798000	0.212002500	0.000799825
83/11/25	1710	120.00	2.041825000	0.387952500	0.266020300	0.050198075	0.063767500	0.337985000	0.000200100
83/11/25	1717	191.25	1.477750000	0.319987500	0.208002800	0.051399825	0.037599250	0.168015000	0.001600225
83/11/25	1723	195.31	0.559992500	0.178020000	0.101972800	0.036599325	0.022200750	0.123970000	0.003999700
83/11/25	1729	250.00	0.779700000	0.222007500	0.185980300	0.043597075	0.019400500	0.168015000	0.000000000
83/11/25	1736	400.00	1.108025000	0.265995000	0.181955300	0.041400575	0.021798250	0.135987500	0.002400050
83/11/25	1742	460.00	1.407600000	0.306015000	0.233992800	0.053797575	0.016002250	0.143980000	0.000799825
83/11/25	1748	446.88	1.163800000	0.299977500	0.216007800	0.050399325	0.007797000	0.066010000	0.000000000
83/11/25	1754	400.00	0.966000000	0.245985000	0.181955300	0.039600825	0.007797000	0.053998250	0.000200100
83/11/25	1801	350.00	1.075825000	0.255990000	0.183967800	0.041199325	0.013000750	0.059972500	0.000999925
83/11/25	1807	250.00	1.107450000	0.270020000	0.195985300	0.045201325	0.002999775	0.065998500	0.000999925
83/12/17	0	0.00	0.000000000	0.000000000	0.054000000	0.000000000	0.000000000	0.014000000	0.000000000

Soluble Stormwater Data (mg/l)

Date	Time	Flow	Iron	Lead	Zinc	Copper	Chromium	Nickel	Cadmium
83/12/17	454	90.00	0.424000000	0.158000000	0.030000000	0.028000000	0.014000000	0.036000000	0.003800000
83/12/17	457	90.00	0.398000000	0.146000000	0.042000000	0.036000000	0.000000000	0.038000000	0.006000000
83/12/17	501	85.00	0.492000000	0.190000000	0.048000000	0.032000000	0.002000000	0.056000000	0.005600000
83/12/17	504	80.00	0.362000000	0.148000000	0.022000000	0.024000000	0.000000000	0.022000000	0.004400000
83/12/17	507	77.34	0.344000000	0.138000000	0.026000000	0.026000000	0.002000000	0.028000000	0.003200000
83/12/17	510	75.63	0.636000000	0.222000000	0.056000000	0.026000000	0.008000000	0.000000000	0.007800000
83/12/17	513	74.84	0.330000000	0.148000000	0.014000000	0.022000000	0.010000000	0.028000000	0.010400000
83/12/17	1101	255.47	0.502000000	0.212000000	0.070000000	0.026000000	0.004000000	0.050000000	0.006400000
83/12/17	1104	333.59	0.766000000	0.388000000	0.118000000	0.040000000	0.012000000	0.068000000	0.004600000
83/12/17	1107	378.32	0.686000000	0.354000000	0.122000000	0.026000000	0.014000000	0.104000000	0.004200000
83/12/17	1110	385.16	0.690000000	0.304000000	0.120000000	0.026000000	0.002000000	0.120000000	0.000000000
83/12/17	1113	385.16	0.584000000	0.326000000	0.100000000	0.038000000	0.004000000	0.094000000	0.000000000
83/12/17	1117	371.88	0.556000000	0.310000000	0.104000000	0.032000000	0.004000000	0.042000000	0.000000000
83/12/17	1120	354.88	0.708000000	0.328000000	0.102000000	0.034000000	0.018000000	0.050000000	0.004400000
84/01/02	0	0.00	0.000000000	0.000000000	0.000000000	0.000000000	0.000000000	0.000000000	0.000000000
84/01/02	1324	105.00	0.977860000	0.125996000	0.132002000	0.028002000	0.013988000	0.085982000	0.000800020
84/01/02	1330	110.00	0.641940000	0.106002000	0.119990000	0.032006000	0.000000000	0.063986000	0.000000000
84/01/02	1336	115.00	0.430040000	0.136006000	0.093990000	0.026000000	0.000000000	0.030004000	0.000000000
84/01/02	1343	110.00	0.655980000	0.188006000	0.125996000	0.032006000	0.000000000	0.006006000	0.000000000
84/01/02	1349	100.00	0.476060000	0.177996000	0.106002000	0.026000000	0.007982000	0.000000000	0.000000000
84/01/02	1355	120.00	0.427960000	0.227994000	0.117988000	0.026000000	0.009999600	0.013988000	0.000000000
84/01/02	1401	130.63	0.430040000	0.199992000	0.108004000	0.024000600	0.000000000	0.000000000	0.000000000
84/01/02	1408	140.00	0.893880000	0.274040000	0.193986000	0.043992000	0.006006000	0.000000000	0.008398000
84/01/02	1414	149.84	0.771940000	0.297960000	0.140010000	0.037986000	0.000000000	0.000000000	0.006994000
84/01/02	1420	191.25	0.647920000	0.251992000	0.099996000	0.024000600	0.003998800	0.000000000	0.000000000
84/01/02	1426	218.75	0.600080000	0.153998000	0.123994000	0.028002000	0.003998800	0.000000000	0.005800600
84/01/02	1433	231.25	0.431860000	0.203996000	0.089986000	0.019999200	0.000000000	0.037986000	0.005400200
84/01/02	1439	243.75	0.581880000	0.163982000	0.132002000	0.032006000	0.009999600	0.054002000	0.007800000
84/01/02	1445	250.00	0.433940000	0.099996000	0.091988000	0.024000600	0.000000000	0.016000400	0.002199860
84/01/02	1452	255.47	0.540020000	0.137982000	0.184002000	0.021998600	0.000000000	0.011999000	0.006598800
84/01/02	1458	261.46	0.594100000	0.253994000	0.110006000	0.026000000	0.006006000	0.024000600	0.000000000
84/01/02	1504	261.46	0.215982000	0.035984000	0.041990000	0.009999600	0.009999600	0.000000000	0.000399880
84/01/02	1510	237.50	0.235976000	0.001999920	0.037986000	0.011999000	0.000000000	0.001999400	0.002600000
84/01/02	1517	206.25	0.307840000	0.030004000	0.039988000	0.014001000	0.011999000	0.006006000	0.008200400
84/01/02	1523	191.25	0.218010000	0.024000600	0.037986000	0.009999600	0.000000000	0.009999600	0.004599400
84/01/02	1529	187.81	0.182000000	0.123994000	0.037986000	0.011999000	0.000000000	0.009999600	0.009599200
84/01/02	1535	191.25	0.159900000	0.084006000	0.035984000	0.011999000	0.000000000	0.030004000	0.016406000
84/01/02	1542	225.00	0.193960000	0.043992000	0.041990000	0.009999600	0.000000000	0.003998800	0.013200200
84/01/02	1548	250.00	0.138008000	0.021998600	0.035984000	0.008000200	0.000000000	0.009999600	0.003601000
84/01/22	0	0.00	0.000000000	0.000000000	0.070000000	0.006000000	0.000000000	0.000000000	0.000000000
84/01/22	1259	90.00	0.618000000	0.144000000	0.122000000	0.032000000	0.002000000	0.045800000	0.002600000
84/01/22	1305	90.00	0.632000000	0.206000000	0.130000000	0.046000000	0.006000000	0.090600000	0.002800000
84/01/22	1311	95.00	0.644000000	0.204000000	0.120000000	0.030000000	0.002000000	0.156000000	0.000600000
84/01/22	1318	100.00	1.136000000	0.238000000	0.162000000	0.040000000	0.058000000	0.134000000	0.003400000
84/01/22	1324	102.50	0.794000000	0.232000000	0.132000000	0.026000000	0.012000000	0.052400000	0.004400000
84/01/22	1330	105.00	0.578000000	0.196000000	0.116000000	0.024000000	0.012000000	0.061800000	0.004600000
84/01/22	1336	110.00	0.534000000	0.178000000	0.116000000	0.026000000	0.004000000	0.032000000	0.005000000
84/01/22	1342	110.00	0.544000000	0.168000000	0.132000000	0.024000000	0.016000000	0.098800000	0.000000000
84/01/22	1348	120.00	0.714000000	0.242000000	0.120000000	0.034000000	0.028000000	0.080200000	0.002000000
84/01/22	1355	120.00	0.572000000	0.238000000	0.100000000	0.022000000	0.008000000	0.016400000	0.001600000
84/01/22	1401	130.63	0.520000000	0.212000000	0.110000000	0.022000000	0.008000000	0.041800000	0.000000000
84/01/22	1407	135.47	0.516000000	0.248000000	0.100000000	0.022000000	0.008000000	0.012400000	0.000000000
84/01/22	1413	135.47	0.500000000	0.232000000	0.096000000	0.022000000	0.014000000	0.004000000	0.000000000

Soluble Stormwater Data (mg/l)

Date	Time	Flow	Iron	Lead	Zinc	Copper	Chromium	Nickel	Cadmium
84/01/22	1419	135.47	0.514000000	0.224000000	0.120000000	0.022000000	0.004000000	0.022000000	0.000000000
84/01/22	1426	140.00	0.522000000	0.226000000	0.096000000	0.024000000	0.010000000	0.031800000	0.000120000
84/01/22	1432	140.00	0.526000000	0.228000000	0.098000000	0.024000000	0.014000000	0.038200000	0.003400000
84/01/22	1438	140.00	0.584000000	0.182000000	0.182000000	0.032000000	0.014000000	0.023200000	0.001800600
84/01/22	1444	140.00	0.424000000	0.200000000	0.080000000	0.022000000	0.002000000	0.033000000	0.000200000
84/01/22	1450	135.47	0.458000000	0.172000000	0.084000000	0.018000000	0.004000000	0.043200000	0.006200000
84/01/22	1457	135.47	0.494000000	0.196000000	0.070000000	0.018000000	0.006000000	0.069000000	0.000000000
84/01/22	1503	135.47	0.420000000	0.132000000	0.064000000	0.018000000	0.006000000	0.038000000	0.000000000
84/01/22	1509	130.63	0.412000000	0.144000000	0.066000000	0.016000000	0.000000000	0.055600000	0.004600000
84/01/22	1515	130.63	0.420000000	0.122000000	0.054000000	0.016000000	0.000000000	0.016400000	0.007000000
84/01/22	1521	120.00	0.492000000	0.156000000	0.082000000	0.018000000	0.000000000	0.008600000	0.001000000
84/05/10	0	0.00	0.073999480	0.000000000	0.014000220	0.000000000	0.000000000	0.000000000	0.000399900
84/05/10	1733	0.00	7.175970520	0.999998000	1.489995780	0.165999420	0.029999940	0.419999780	0.015199920
84/05/10	1737	0.00	4.421998720	1.099997800	1.041996180	0.117999640	0.014000220	0.059999880	0.011600200
84/05/10	1742	0.00	3.929997720	0.620000000	0.569999480	0.099999800	0.054000140	0.419999780	0.004000240
84/05/10	1746	0.00	2.553994520	0.639995000	0.597999300	0.081999960	0.005999740	0.139999720	0.002600280
84/05/10	1750	0.00	6.159976520	0.879997000	1.005998980	0.057999760	0.047999780	0.519999580	0.005999740
84/05/10	1754	0.00	6.977942520	1.399997200	1.493994780	0.127999620	0.027999820	0.539999540	0.009800340
84/05/10	1758	0.00	2.940000320	0.999998000	1.271997580	0.171999780	0.049999900	0.219999560	0.005000300
84/05/10	1802	0.00	2.940000320	0.799998400	0.885997980	0.145999460	0.027999820	0.399999820	0.002200380
84/05/10	1806	0.00	2.903996920	0.620000000	0.697995380	0.159999680	0.019999960	0.379999860	0.006200000
84/05/10	1810	0.00	5.367994720	0.659996200	0.595999180	0.119999760	0.025999700	0.419999780	0.003400080
84/05/10	1814	0.00	3.071998320	0.519999580	0.525999320	0.131999860	0.047999780	0.419999780	0.006599900
84/05/10	1818	0.00	2.361999120	0.459999700	0.493999260	0.131999860	0.034000180	0.659996200	0.003799980
84/05/10	1822	0.00	1.685994520	0.359999900	0.405999560	0.111999900	0.000000000	0.039999920	0.006999800
84/05/10	1826	0.00	1.499994520	0.299999400	0.425999520	0.103999420	0.012000100	0.199999600	0.000399900
84/05/10	1830	0.00	1.635997720	0.279999440	0.425999520	0.099999800	0.004000240	0.239999520	0.004600400
84/05/10	1834	0.00	1.087998320	0.219999560	0.331999460	0.087999700	0.000000000	0.239999520	0.003400080
84/05/10	1838	0.00	1.013995120	0.259999480	0.493999260	0.091999940	0.000000000	0.099999800	0.007599960
84/05/10	1842	0.00	0.925998520	0.199999600	0.353999540	0.097999680	0.015999720	0.259999480	0.007400320
84/05/10	1846	0.00	0.827995120	0.179999640	0.307999260	0.083999460	0.000000000	0.199999600	0.006800160
84/05/10	1848	0.00	1.221998920	0.159999680	0.277999320	0.087999700	0.151999820	1.059995400	0.007800220
84/05/24	0	0.00	0.000000000	0.000000000	0.004000240	0.000000000	0.000000000	0.000000000	0.002199760
84/05/24	1540	2012.54	5.929996200	1.319998600	1.011993760	0.077999720	0.015999720	0.127999620	0.014600380
84/05/24	1548	1550.00	3.395994200	0.899998200	0.647997960	0.101999920	0.014000220	0.155999440	0.005400200
84/05/24	1556	1300.00	2.435998600	0.939994400	0.667999160	0.093999440	0.007999860	0.057999760	0.012000100
84/05/24	1605	586.25	1.529998800	0.479999660	0.415999540	0.042000040	0.005999740	0.036000300	0.007800840
84/05/24	1613	400.00	0.801994800	0.299999400	0.301999520	0.044000160	0.002000120	0.024000200	0.000800420
84/05/24	1621	191.25	0.841997200	0.199999600	0.219999560	0.039999920	0.002000120	0.027999820	0.000400520
84/05/24	1629	110.00	0.615999760	0.159999680	0.199999600	0.042000040	0.005999740	0.022000080	0.006400260
84/05/24	1638	446.88	0.683996400	0.199999600	0.197999480	0.039999920	0.005999740	0.017999840	0.000000000
84/05/24	1646	365.82	0.807996400	0.219999560	0.221999680	0.046000280	0.005999740	0.009999980	0.000000000
84/05/24	1654	250.00	0.617999880	0.199999600	0.245999260	0.046000280	0.004000240	0.000000000	0.002600280
84/05/24	1703	163.91	0.763995000	0.299999400	0.255999240	0.044000160	0.004000240	0.000000000	0.003600340
84/05/24	1711	110.00	0.517999460	0.139999720	0.149999700	0.034000180	0.002000120	0.000000000	0.002200380
84/05/25	0	0.00	0.000000000	0.000000000	0.004000240	0.000000000	0.000000000	0.000000000	0.002199760
84/05/25	2233	120.00	0.337999820	0.019999960	0.139999720	0.027999820	0.005999740	0.049999900	0.000000000
84/05/25	2237	125.47	0.331999460	0.059999880	0.405999560	0.036000300	0.005999740	0.024000200	0.004000240
84/05/25	2245	135.47	0.267999960	0.039999920	0.113999400	0.025999700	0.000799800	0.022000080	0.003400080
84/05/25	2253	140.00	0.167999540	0.059999880	0.121999260	0.027999820	0.002000120	0.019999960	0.000600160
84/05/25	2301	142.34	0.203999840	0.079999840	0.093999440	0.029999940	0.002000120	0.000000000	0.001800480
84/05/25	2309	191.25	0.131999860	0.079999840	0.091999320	0.024000260	0.002000120	0.000000000	0.001800480
84/05/25	2317	261.46	0.205999960	0.059999880	0.083999460	0.024000200	0.000000000	0.000000000	0.000000000

Soluble Stormwater Data (mg/l)

Date	Time	Flow	Iron	Lead	Zinc	Copper	Chromium	Nickel	Cadmium
84/05/25	2325	250.00	0.171999780	0.059999880	0.079999220	0.024000200	0.007999860	0.029999940	0.000800420
84/05/25	2334	206.25	0.145999460	0.039999920	0.069999240	0.017999840	0.002000120	0.005999740	0.004800040
84/05/25	2342	155.00	0.191999740	0.039999920	0.097999680	0.019999960	0.005999740	0.000000000	0.000000000
84/05/25	2350	120.00	0.181999760	0.079999840	0.081999340	0.017999840	0.002000120	0.000000000	0.002000120
84/06/20	0	0.00	0.000000000	0.000000000	0.000000000	0.000000000	0.000000000	0.000000000	0.000000000
84/06/20	50	90.00	2.005997600	0.659998200	0.731996800	0.099999800	0.009999980	0.096599720	0.004599780
84/06/20	54	195.31	2.125998600	0.539999540	0.713998200	0.087999700	0.017999840	0.052600180	0.006999800
84/06/20	1612	140.00	1.133998600	0.219999560	0.265999840	0.054000140	0.034000180	0.283799420	0.000000000
84/06/20	1617	77.34	3.063996600	0.479999660	0.459999700	0.141999840	0.075999600	0.677598000	0.006599900
84/06/20	1621	120.00	4.009998300	0.499999620	0.511999720	0.119999760	0.105999540	0.711195800	0.001799860
84/06/20	1628	90.00	1.833997200	0.299999400	0.341999440	0.075999600	0.007999860	0.127199820	0.005400200
84/06/20	1632	74.84	2.827999800	0.419999780	0.409999800	0.071999980	0.077999720	0.603599760	0.004800040
84/06/20	1827	558.83	2.121999600	0.519999580	0.459999700	0.077999720	0.034000180	0.327799580	0.005400200
84/06/20	1831	465.63	3.251999200	0.699998600	0.699978600	0.117999640	0.039999920	0.303399480	0.005599840
84/06/20	1835	365.82	1.253999600	0.399999820	0.387999720	0.067999740	0.004000240	0.028999880	0.003799980
84/06/20	1839	306.05	2.217994200	0.559999500	0.541999660	0.099999800	0.019999960	0.172399680	0.001799860
84/06/20	1843	237.50	3.481994400	0.620000000	0.701995000	0.113999400	0.077999720	0.530799980	0.006599900
84/06/20	1848	171.88	3.165999000	0.639995000	0.627998000	0.113999400	0.036000300	0.390399740	0.004400140
84/06/20	1852	120.00	1.798000000	0.439999740	0.403999440	0.077999720	0.005999740	0.106199800	0.005599840
84/06/20	1855	100.00	3.165999000	0.459999700	0.489999640	0.085999580	0.005999740	0.053399980	0.004000240
84/07/15	0	0.00	0.000000000	0.000000000	0.005999740	0.000000000	0.009999980	0.000000000	0.000200260
84/07/15	1132	200.00	0.219999560	0.079999840	0.116000140	0.009999980	0.000000000	0.040399820	0.003199820
84/07/15	1136	191.25	0.195999980	0.079999840	0.109999780	0.007999860	0.000000000	0.103799780	0.001999500
84/07/15	1140	171.88	0.161999600	0.099999800	0.109999780	0.004000240	0.000000000	0.000000000	0.004399520
84/07/15	1144	187.81	0.181999760	0.059999880	0.077999720	0.009999980	0.000000000	0.014599760	0.004399520
84/07/15	1148	163.91	0.079999840	0.059999880	0.071999980	0.002000120	0.000000000	0.000000000	0.006399640
84/07/15	1152	115.00	0.139999720	0.039999920	0.106000160	0.005999740	0.002000120	0.015999720	0.004599780
84/07/15	1156	90.00	0.139999720	0.159999680	0.087999700	0.009999980	0.000000000	0.045400120	0.000798740

Total Stormwater Data (mg/l)

Date	Time	Flow	Iron	Lead	Zinc	Copper	Chromium	Nickel	Cadmium
83/08/16	2305	155.00	6.4900	0.6690	0.7580	0.2200	0.0815	1.4750	0.01520
83/08/16	2308	163.91	8.3935	0.9890	1.0375	0.2325	0.0455	0.6750	0.00000
83/08/16	2312	212.50	14.1935	0.6555	1.3175	0.2750	0.0710	0.0050	0.01520
83/08/16	2315	206.25	15.3185	2.1850	1.4325	0.2790	0.1590	0.3395	0.00000
83/08/16	2318	200.00	10.6685	1.2180	1.4260	0.2420	0.0485	0.8800	0.00000
83/08/16	2321	191.25	10.6185	0.2865	0.8785	0.1675	0.1755	0.0500	0.02250
83/08/16	2324	163.91	8.2440	0.3410	0.7175	0.1735	0.1220	0.0000	0.00000
83/08/16	2328	145.63	9.8685	0.2395	0.7120	0.1740	0.0350	0.7250	0.00145
83/08/16	2331	130.63	7.3760	0.5050	0.7840	0.2245	0.2130	0.5500	0.04250
83/08/16	2334	115.00	6.6245	0.4975	0.8005	0.3165	0.0895	0.4750	0.00000
83/08/16	2337	105.00	6.2300	0.4435	0.6495	0.1380	0.1420	0.0000	0.01250
83/08/16	2340	95.00	4.6805	0.5255	0.4470	0.1120	0.0215	0.4775	0.05295
83/08/16	2344	85.00	3.2760	0.7700	0.6910	0.1610	0.0565	0.0250	0.00015
83/08/16	2347	85.00	4.1475	0.2065	0.4345	0.1300	0.0080	0.3000	0.00000
83/08/16	2350	85.00	4.9740	0.4014	0.6860	0.1565	0.1330	1.3500	0.01250
83/09/16	1546	90.00	5.7960	0.5218	0.3708	0.0767	0.0163	0.0669	0.00433
83/09/16	1550	250.00	7.4649	0.3672	0.4433	0.0919	0.0269	0.0726	0.00243
83/09/16	1554	586.25	7.5507	0.3699	0.3808	0.0795	0.0325	0.0320	0.00332
83/09/16	1557	333.59	5.0379	0.2158	0.2194	0.1531	0.0207	0.0273	0.00312
83/09/16	1600	296.09	6.0261	0.2415	0.2175	0.0633	0.0236	0.0480	0.00275
83/09/16	1603	250.00	4.8276	0.4592	0.2770	0.0645	0.0229	0.0786	0.00625
83/09/16	1608	191.25	2.7895	0.2594	0.1788	0.0384	0.0097	0.2906	0.00538
83/09/16	1611	187.81	2.0377	0.1737	0.0967	0.0284	0.0134	0.0373	0.00091
83/09/16	1614	163.91	2.1015	0.1654	0.2994	0.0242	0.0051	0.0445	0.00050
83/09/16	1617	140.00	1.7043	0.1692	0.0660	0.0129	0.0088	0.0542	0.00650
83/09/16	1621	115.00	1.6548	0.1444	0.1053	0.0215	0.0231	0.1164	0.00749
83/09/16	1624	90.00	1.8009	0.1868	0.1525	0.0274	0.0113	0.0105	0.00270
83/10/10	512	140.00	1.5897	0.1168	0.1782	0.0387	0.0036	0.0000	0.00108
83/10/10	518	105.00	2.1779	0.2145	0.1090	0.0346	0.0218	0.0000	0.00005
83/10/10	524	90.00	1.6640	0.1337	0.1897	0.0629	0.0339	0.2030	0.00470
83/10/10	530	125.47	1.0102	0.0402	0.0893	0.0239	0.2457	0.2458	0.00108
83/10/10	537	95.00	1.0086	0.0815	0.3047	0.0219	0.0032	0.0127	0.00648
83/10/10	543	77.34	1.0406	0.0810	0.5756	0.0248	0.0018	0.0392	0.00935
83/10/10	549	74.84	1.0610	0.1450	0.0976	0.0316	0.0110	0.0269	0.00460
83/10/10	614	250.00	0.7909	0.0524	0.0734	0.0407	0.0171	0.0544	0.00020
83/10/10	620	324.80	0.9494	0.1051	0.2583	0.0315	0.0137	0.0122	0.00032
83/10/10	627	365.82	1.3842	0.0492	0.0657	0.0235	0.0126	0.0252	0.00092
83/10/10	633	315.63	1.5631	0.1669	0.1033	0.0443	0.0121	0.0000	0.00068
83/10/10	639	250.00	1.5460	0.0796	0.1080	0.0328	0.0079	0.0266	0.00150
83/10/10	646	191.25	1.7320	0.1436	0.1193	0.0527	0.0032	0.0170	0.00637
83/10/10	652	195.31	1.2630	0.1580	0.1440	0.0894	0.0150	0.0844	0.00633
83/10/10	658	243.75	0.9290	0.1631	0.0830	0.0354	0.0018	0.0358	0.00119
83/10/10	704	285.74	0.9736	0.2684	0.0937	0.0469	0.0036	0.0290	0.00100
83/10/10	711	493.75	1.0634	0.1364	0.1146	0.0398	0.0138	0.0219	0.00220
83/10/10	717	531.25	1.3000	0.1427	0.1055	0.0254	0.0136	0.0140	0.00000
83/10/10	723	446.88	1.0703	0.1601	0.0626	0.0142	0.0091	0.0235	0.00048
83/10/10	730	400.00	0.9451	0.0999	0.0884	0.0331	0.0053	0.0238	0.00130
83/10/10	736	333.59	1.0677	0.1523	0.0931	0.0248	0.0039	0.0732	0.00869
83/10/10	742	275.00	0.8618	0.0871	0.0635	0.0229	0.0119	0.0246	0.00440
83/10/10	749	218.75	0.8230	0.0944	0.0926	0.0268	0.0075	0.0192	0.01499
83/10/10	755	187.81	0.5860	0.0713	0.0597	0.0244	0.0066	0.0000	0.00339
83/10/10	801	163.91	0.8494	0.1263	0.0688	0.0230	0.0052	0.0052	0.00000
83/11/02	1730	493.75	14.7947	0.7650	0.0240	0.2625	0.1275	0.7305	0.00225

Total Stormwater Data (mg/l)

Date	Time	Flow	Iron	Lead	Zinc	Copper	Chromium	Nickel	Cadmium
83/11/02	1733	400.00	15.6050	0.7345	0.0225	0.1780	0.1345	0.8312	0.00635
83/11/02	1736	333.59	16.9790	0.8258	0.0275	0.1465	0.0680	0.2838	0.00770
83/11/02	1739	218.75	16.6790	0.7830	0.0285	0.1315	0.0730	0.3954	0.00130
83/11/02	1746	285.74	15.9370	0.7755	0.0265	0.1265	0.0720	0.3800	0.00689
83/11/02	1753	191.25	33.4730	1.2507	0.0650	0.2140	0.0845	0.2425	0.00875
83/11/02	1758	163.91	18.2070	0.6205	0.0195	0.1070	0.0355	0.1223	0.00395
83/11/02	1800	140.00	3.3171	0.2955	0.0045	0.0545	0.0680	0.5860	0.00485
83/11/02	1807	90.00	2.3177	0.2814	0.0115	0.0510	0.0350	0.3332	0.00274
83/11/03	20	218.75	1.7728	0.1160	0.0025	0.0300	0.1260	1.4116	0.00115
83/11/03	26	191.25	1.6847	0.1200	0.0025	0.1860	0.1960	1.5233	0.00279
83/11/03	32	200.00	3.6699	0.2900	0.0070	0.0575	0.0385	0.2297	0.00245
83/11/03	39	206.25	2.9930	0.2515	0.0045	0.0420	0.0200	0.1123	0.00075
83/11/03	45	163.91	1.9304	0.1525	0.0025	0.0315	0.0290	0.2807	0.00020
83/11/03	51	140.00	1.5140	0.1185	0.0025	0.0455	0.0350	0.2898	0.00045
83/11/03	58	130.63	1.0327	0.0715	0.0005	0.0255	0.0275	0.1423	0.00155
83/11/03	107	110.00	0.8184	0.0475	0.0000	0.0185	0.0130	0.1157	0.00046
83/11/03	110	95.00	0.3240	0.0496	0.0034	0.0207	0.0138	0.0196	0.00056
83/11/03	212	95.00	0.3590	0.0695	0.0000	0.0160	0.0080	0.0573	0.00095
83/11/03	216	90.00	0.3128	0.0350	0.0000	0.0160	0.0080	0.0908	0.00085
83/11/25	1521	135.47	2.6387	0.3182	0.1944	0.0594	0.0513	0.3999	0.00080
83/11/25	1524	140.00	2.1087	0.2713	0.1599	0.0511	0.0365	0.2600	0.00162
83/11/25	1527	142.34	2.6626	0.3813	0.1917	0.0641	0.0327	0.2840	0.00120
83/11/25	1530	145.63	2.2722	0.3123	0.1675	0.0559	0.0436	0.2840	0.00220
83/11/25	1536	142.34	1.7223	0.1982	0.1078	0.0400	0.0451	0.1960	0.00040
83/11/25	1543	145.63	1.1707	0.1672	0.0827	0.0321	0.0447	0.2442	0.00263
83/11/25	1549	142.34	1.1674	0.2119	0.1118	0.0408	0.0368	0.1876	0.00229
83/11/25	1555	140.00	1.2970	0.2400	0.1259	0.0468	0.0452	0.2220	0.00208
83/11/25	1602	135.47	1.1526	0.2558	0.1359	0.0447	0.0360	0.1860	1.54570
83/11/25	1608	130.63	1.2713	0.1967	0.1045	0.0347	0.0347	0.1619	0.00000
83/11/25	1614	120.00	4.5820	0.6270	0.3387	0.0997	0.0329	0.1140	0.00153
83/11/25	1620	110.00	4.8400	0.5420	0.3620	0.0970	0.0503	0.2700	0.00155
83/11/25	1627	90.00	5.0977	0.5304	0.3913	0.1001	0.0393	0.2300	0.00167
83/11/25	1651	95.00	5.4740	0.4970	0.3996	0.1013	0.1166	0.4840	0.00219
83/11/25	1658	100.00	5.0046	0.5103	0.3553	0.0938	0.0629	0.3140	0.00234
83/11/25	1704	95.00	4.2707	0.4283	0.3087	0.0777	0.0470	0.2285	0.00089
83/11/25	1710	120.00	3.3950	0.4252	0.2877	0.0730	0.0793	0.3384	0.00029
83/11/25	1717	191.25	2.8587	0.3483	0.2240	0.0615	0.0469	0.1680	0.00042
83/11/25	1723	195.31	1.2866	0.1872	0.1098	0.0411	0.0290	0.1240	0.00403
83/11/25	1729	250.00	1.9820	0.2353	0.2016	0.0507	0.0248	0.1680	0.00022
83/11/25	1736	400.00	2.6031	0.2932	0.2045	0.0544	0.0310	0.1359	0.00244
83/11/25	1742	400.00	3.2640	0.3420	0.2678	0.0765	0.0297	0.1536	0.00106
83/11/25	1748	446.88	2.8408	0.3272	0.2436	0.0646	0.0169	0.0660	0.00009
83/11/25	1754	400.00	2.4560	0.2690	0.2036	0.0513	0.0165	0.0540	0.00050
83/11/25	1801	350.00	2.5345	0.2732	0.2075	0.0534	0.0204	0.0599	0.00143
83/11/25	1807	250.00	2.7662	0.2863	0.2151	0.0539	0.0082	0.0659	0.00104
83/12/17	454	90.00	0.9710	0.1586	0.0337	0.0286	0.0159	0.0360	0.00492
83/12/17	457	90.00	0.8870	0.1460	0.0464	0.0379	0.0025	0.0380	0.00894
83/12/17	501	85.00	0.9936	0.1900	0.0517	0.0332	0.0039	0.0560	0.00804
83/12/17	504	80.00	0.7760	0.1505	0.0245	0.0012	0.0025	0.0220	0.00440
83/12/17	507	77.34	0.6780	0.1380	0.0279	0.0032	0.0064	0.0280	0.00564
83/12/17	510	75.63	1.1290	0.2226	0.0604	0.0092	0.0130	0.0000	0.00905
83/12/17	513	74.84	0.5550	0.1492	0.0140	0.0106	0.0100	0.0280	0.01040
83/12/17	1101	255.47	1.9300	0.2501	0.0875	0.0316	0.0077	0.0500	0.00696

Total Stormwater Data (mg/l)

Date	Time	Flow	Iron	Lead	Zinc	Copper	Chromium	Nickel	Cadmium
83/12/17	1104	333.59	2.9920	0.4174	0.1480	0.0475	0.0201	0.0680	0.00516
83/12/17	1107	378.32	3.4980	0.3790	0.1620	0.0354	0.0295	0.1040	0.00439
83/12/17	1110	385.16	3.6130	0.3421	0.0451	0.0329	0.0163	0.1237	0.00000
83/12/17	1113	385.16	4.1460	0.3654	0.1406	0.0474	0.0214	0.0952	0.00000
83/12/17	1117	371.88	3.2830	0.3500	0.1327	0.0382	0.0152	0.0000	0.00000
83/12/17	1120	354.89	3.5900	0.3567	0.1332	0.0115	0.1280	0.0044	0.00465
84/01/02	1324	105.00	1.3198	0.1356	0.1387	0.0318	0.0246	0.0946	0.00128
84/01/02	1330	110.00	0.7709	0.1243	0.1257	0.0349	0.0019	0.1070	0.00000
84/01/02	1336	115.00	0.5989	0.1360	0.1007	0.0298	0.0038	0.0415	0.00000
84/01/02	1343	110.00	0.7740	0.1947	0.1337	0.0349	0.0038	0.0060	0.00961
84/01/02	1349	100.00	0.6901	0.1923	0.1117	0.0279	0.0176	0.0673	0.00327
84/01/02	1355	120.00	0.5799	0.2289	0.1228	0.0279	0.0157	0.0140	0.00000
84/01/02	1401	130.63	0.6159	0.1999	0.1128	0.0288	0.0000	0.0000	0.00000
84/01/02	1408	140.00	1.0638	0.2980	0.2007	0.0478	0.0070	0.0000	0.00945
84/01/02	1414	149.84	1.0089	0.3056	0.1466	0.0408	0.0000	0.0000	0.00718
84/01/02	1420	191.25	0.8829	0.2616	0.1047	0.0259	0.0059	0.0000	0.00259
84/01/02	1426	218.75	0.6220	0.1540	0.1288	0.0299	0.0040	0.0000	0.00816
84/01/02	1433	231.25	0.6738	0.2097	0.0946	0.0229	0.0000	0.0380	0.00915
84/01/02	1439	243.75	0.8888	0.1640	0.1368	0.0339	0.0100	0.0540	0.01126
84/01/02	1445	250.00	0.7238	0.0999	0.0987	0.0259	0.0019	0.0179	0.00220
84/01/02	1452	255.47	0.7910	0.1380	0.1897	0.0309	0.0000	0.0129	0.00822
84/01/02	1458	261.46	0.8550	0.2587	0.1167	0.0288	0.0127	0.0240	0.00000
84/01/02	1504	261.46	0.3699	0.0360	0.0477	0.0108	0.0205	0.0067	0.00385
84/01/02	1510	237.50	0.4929	0.0068	0.0428	0.0130	0.0010	0.0020	0.00366
84/01/02	1517	206.25	0.5357	0.0299	0.0467	0.0159	0.0168	0.0060	0.01309
84/01/02	1523	191.25	0.4419	0.0240	0.0437	0.0109	0.0115	0.0196	0.00575
84/01/02	1529	187.81	0.4040	0.1268	0.0437	0.0218	0.0077	0.0100	0.01315
84/01/02	1535	191.25	0.3666	0.0868	0.0417	0.0139	0.0048	0.0300	0.01640
84/01/02	1542	225.00	0.4459	0.0440	0.0468	0.0119	0.0019	0.0040	0.01483
84/01/02	1548	250.00	0.3840	0.0258	0.0128	0.0099	0.0058	0.0100	0.00360
84/01/22	1259	90.00	3.3550	0.1623	0.1582	0.0379	0.0138	0.0473	0.00260
84/01/22	1305	90.00	3.0550	0.2287	0.1632	0.0511	0.0176	0.0917	0.00341
84/01/22	1311	95.00	4.4960	0.2424	0.1741	0.0408	0.0208	0.1613	0.00060
84/01/22	1318	100.00	3.7680	0.2747	0.1977	0.0442	0.0733	0.1383	0.00340
84/01/22	1324	102.50	3.2889	0.2398	0.1652	0.0301	0.0262	0.0626	0.00597
84/01/22	1330	105.00	2.9295	0.2160	0.1460	0.0282	0.0201	0.0618	0.00460
84/01/22	1336	110.00	2.8474	0.2030	0.1472	0.0312	0.0092	0.0372	0.00500
84/01/22	1342	110.00	2.4994	0.1942	0.1566	0.0290	0.0224	0.0976	0.00000
84/01/22	1348	120.00	2.9940	0.2825	0.1475	0.0423	0.0411	0.0802	0.00200
84/01/22	1355	120.00	2.6942	0.2646	0.1281	0.0275	0.0188	0.0224	0.00200
84/01/22	1401	130.63	1.4337	0.2259	0.1363	0.0261	0.0148	0.0542	0.00041
84/01/22	1407	135.47	2.3330	0.2903	0.1235	0.0244	0.0118	0.0124	0.00078
84/01/22	1413	135.47	2.6956	0.2444	0.1246	0.0271	0.0167	0.0040	0.00119
84/01/22	1419	135.47	2.2424	0.2505	0.1422	0.0244	0.0073	0.0220	0.00100
84/01/22	1426	140.00	3.7377	0.2598	0.1396	0.0300	0.0245	0.0365	0.00012
84/01/22	1432	140.00	2.2202	0.2480	0.1180	0.0261	0.0173	0.0382	0.00340
84/01/22	1438	140.00	2.5740	0.1995	0.2056	0.0351	0.0167	0.0232	0.00180
84/01/22	1444	140.00	1.8527	0.2177	0.0968	0.0243	0.0040	0.0426	0.00138
84/01/22	1450	135.47	1.7819	0.1912	0.1010	0.0209	0.0067	0.0469	0.00745
84/01/22	1457	135.47	1.7901	0.2093	0.0861	0.0192	0.0093	0.0767	0.00129
84/01/22	1503	135.47	1.4688	0.1331	0.0798	0.0205	0.0128	0.0457	0.00000
84/01/22	1509	130.63	1.5849	0.1528	0.0769	0.0164	0.0048	0.0590	0.00596
84/01/22	1515	130.63	1.5277	0.1317	0.0731	0.0212	0.0046	0.0171	0.00742

Total Stormwater Data (mg/l)

Date	Time	Flow	Iron	Lead	Zinc	Copper	Chromium	Nickel	Cadmium
84/01/22	1521	120.00	1.4324	0.1770	0.0958	0.0183	0.0020	0.0127	0.00124
84/05/24	1540	2012.54	20.4860	1.9932	1.3615	0.2925	0.0886	0.1792	0.01944
84/05/24	1548	1550.00	13.6177	1.1620	0.8556	0.1923	0.0648	0.1886	0.00834
84/05/24	1556	1300.00	10.9234	1.1819	0.8656	0.1734	0.0475	0.0842	0.01405
84/05/24	1605	586.25	8.4755	0.7581	0.6019	0.1247	0.0403	0.0533	0.00998
84/05/24	1613	400.00	4.6971	0.3402	0.3532	0.0577	0.0133	0.0401	0.00840
84/05/24	1621	191.25	4.2539	0.2160	0.2626	0.0536	0.0105	0.0412	0.00040
84/05/24	1629	110.00	3.6906	0.1721	0.2346	0.0525	0.0153	0.0389	0.00700
84/05/24	1638	446.88	3.0166	0.2160	0.2298	0.0480	0.0124	0.0248	0.00012
84/05/24	1646	365.62	4.6064	0.2448	0.2684	0.0573	0.0169	0.0251	0.00044
84/05/24	1654	250.00	3.0595	0.2160	0.2774	0.0541	0.0104	0.0105	0.00260
84/05/24	1703	163.91	4.3586	0.3402	0.3084	0.0601	0.0153	0.0097	0.00360
84/05/24	1711	110.00	2.7216	0.1480	0.1769	0.0417	0.0084	0.0000	0.00337
84/05/25	2233	120.00	0.6811	0.0240	0.1447	0.0300	0.0072	0.0499	0.00048
84/05/25	2237	125.47	0.8461	0.0599	0.4112	0.0384	0.0076	0.0304	0.00448
84/05/25	2245	135.47	0.8285	0.0399	0.1192	0.0284	0.0008	0.0244	0.00412
84/05/25	2253	140.00	0.7019	0.0599	0.1268	0.0296	0.0024	0.0220	0.00173
84/05/25	2301	142.34	0.8491	0.0799	0.0992	0.0323	0.0028	0.0000	0.00261
84/05/25	2309	191.25	0.6804	0.0799	0.0964	0.0256	0.0048	0.0000	0.00228
84/05/25	2317	261.46	0.6749	0.0599	0.0896	0.0256	0.0016	0.0000	0.00040
84/05/25	2325	250.00	0.4829	0.0599	0.0828	0.0252	0.0088	0.0320	0.00189
84/05/25	2334	206.25	0.4524	0.0400	0.0728	0.0200	0.0024	0.0092	0.00480
84/05/25	2342	155.00	0.5681	0.0399	0.1052	0.0212	0.0068	0.0000	0.00036
84/05/25	2350	120.00	0.5118	0.0799	0.0860	0.0192	0.0024	0.0028	0.01611
84/06/20	50	90.00	10.1435	0.8494	0.8735	0.1724	0.0414	0.1180	0.00459
84/06/20	54	195.31	8.6959	0.7092	0.8801	0.1555	0.0410	0.0657	0.00699
84/06/20	1612	140.00	2.6674	0.2366	0.2856	0.0664	0.0469	0.2869	0.00000
84/06/20	1617	77.34	7.0905	0.5242	0.5378	0.1777	0.1103	0.6922	0.00704
84/06/20	1621	120.00	8.7200	0.5483	0.5764	0.1671	0.1503	0.7201	0.00873
84/06/20	1628	90.00	6.1327	0.3483	0.3936	0.1078	0.0245	0.1272	0.00540
84/06/20	1632	74.84	7.5461	0.5005	0.4679	0.1159	0.1147	0.6082	0.00480
84/06/20	1827	558.83	9.2978	0.6973	0.5568	0.1154	0.1017	0.3493	0.00552
84/06/20	1831	465.63	11.9620	0.7967	0.8438	0.1594	0.0876	0.3324	0.00728
84/06/20	1835	365.82	10.0400	0.5370	0.5182	0.1123	0.0363	0.0480	0.00497
84/06/20	1839	306.05	10.0107	0.6486	0.6400	0.1386	0.0522	0.1872	0.00179
84/06/20	1843	237.50	10.2767	0.6764	0.7794	0.1462	0.1114	0.5463	0.00660
84/06/20	1848	171.88	9.7510	0.6993	0.7018	0.1421	0.0691	0.4147	0.00440
84/06/20	1852	120.00	8.2050	0.5085	0.4842	0.1073	0.0334	0.1275	0.00560
84/06/20	1855	100.00	7.7430	0.4922	0.5399	0.1044	0.0765	0.0706	0.00400
84/07/15	1132	200.00	3.4098	0.2452	0.2031	0.0475	0.0141	0.0496	0.00412
84/07/15	1136	191.25	3.8898	0.2250	0.1813	0.0294	0.0157	0.1152	0.00268
84/07/15	1140	171.88	3.0554	0.1966	0.1732	0.0225	0.0117	0.0037	0.00440
84/07/15	1144	187.81	2.0944	0.1244	0.1203	0.0208	0.0089	0.0244	0.00504
84/07/15	1148	163.91	1.6638	0.1204	0.1066	0.0129	0.0048	0.0036	0.00745
84/07/15	1152	115.00	2.1580	0.1246	0.1431	0.0177	0.0105	0.0160	0.00480
84/07/15	1156	90.00	2.2650	0.2244	0.1259	0.0216	0.0072	0.0590	0.00926

Phox System Data

Date	Time	Flow	DO	pH	Temperature	Chloride	Conductivity	Turbidity
83/09/16	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
83/09/16	1546	90.00	19.50	7.40	17.30	540.00	0.00	0.00
83/09/16	1550	250.00	19.90	5.90	17.20	620.00	0.00	140.00
83/09/16	1554	586.[illegible]5	18.20	5.90	17.40	625.00	0.00	440.00
83/09/16	1557	333.59	18.00	6.40	17.50	620.00	0.00	400.00
83/09/16	1600	296.09	18.00	6.40	17.60	600.00	0.00	500.00
83/09/16	1603	250.00	17.90	6.40	17.60	615.00	0.00	360.00
83/09/16	1608	191.25	17.30	6.30	17.70	600.00	0.00	300.00
83/09/16	1611	187.81	17.10	6.30	17.50	620.00	0.00	290.00
83/09/16	1614	163.91	17.10	6.30	17.70	610.00	0.00	250.00
83/09/16	1617	140.00	17.00	6.30	17.90	620.00	0.00	210.00
83/09/16	1621	115.00	16.80	6.30	18.00	625.00	0.00	220.00
83/09/16	1624	90.00	16.50	6.30	17.50	620.00	0.00	250.00
83/10/10	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
83/10/10	512	140.00	10.20	7.20	15.00	840.00	19.00	200.00
83/10/10	518	105.00	10.00	7.30	15.00	840.00	19.00	0.00
83/10/10	524	90.00	10.10	7.40	15.25	835.00	18.00	0.00
83/10/10	530	125.47	10.40	7.40	15.50	840.00	20.00	75.00
83/10/10	537	95.00	10.40	7.40	15.50	845.00	20.00	25.00
83/10/10	543	77.34	10.30	7.50	15.50	847.00	18.00	25.00
83/10/10	549	74.84	10.30	7.40	15.50	820.00	18.00	25.00
83/10/10	614	250.00	10.50	7.40	15.25	800.00	10.00	0.00
83/10/10	620	324.80	11.00	7.40	15.25	780.00	10.00	0.00
83/10/10	627	365.82	11.10	7.30	15.00	725.00	20.00	0.00
83/10/10	633	315.63	11.00	7.30	15.00	740.00	19.00	0.00
83/10/10	639	250.00	11.00	7.30	15.25	740.00	20.00	50.00
83/10/10	646	191.25	11.20	7.30	15.25	700.00	10.00	100.00
83/10/10	652	195.31	11.20	7.30	15.25	700.00	19.00	150.00
83/10/10	658	243.75	11.30	7.30	15.25	690.00	20.00	0.00
83/10/10	704	285.74	11.30	7.30	15.20	680.00	8.00	0.00
83/10/10	711	493.75	11.40	7.30	15.00	660.00	20.00	150.00
83/10/10	717	531.25	11.00	7.20	14.50	650.00	20.00	0.00
83/10/10	723	446.88	11.00	7.20	14.50	640.00	20.00	0.00
83/10/10	730	400.00	11.10	7.20	15.00	640.00	30.00	90.00
83/10/10	736	333.59	11.00	7.20	15.00	640.00	20.00	120.00
83/10/10	742	275.00	11.00	7.20	15.00	640.00	20.00	170.00
83/10/10	749	218.75	11.00	7.20	15.00	630.00	10.00	0.00
83/10/10	755	187.81	11.00	7.20	15.10	640.00	10.00	175.00
83/10/10	801	163.91	11.00	7.20	15.20	650.00	10.00	200.00
83/11/25	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
83/11/25	1521	135.47	0.00	5.20	13.00	670.00	30.00	480.00
83/11/25	1524	140.00	0.00	5.10	13.10	680.00	30.00	250.00
83/11/25	1527	142.34	0.00	5.10	13.25	680.00	30.00	240.00
83/11/25	1530	145.63	0.00	5.15	13.40	690.00	30.00	250.00
83/11/25	1536	142.34	0.00	5.15	13.60	700.00	30.00	275.00
83/11/25	1543	145.63	0.00	5.15	13.00	700.00	30.00	280.00
83/11/25	1549	142.34	0.00	5.15	13.50	700.00	30.00	275.00
83/11/25	1555	140.00	0.00	5.15	13.90	700.00	30.00	240.00
83/11/25	1602	135.47	0.00	5.15	13.50	700.00	30.00	200.00
83/11/25	1608	130.63	0.00	5.15	13.60	705.00	30.00	140.00
83/11/25	1614	120.00	0.00	5.15	14.20	710.00	30.00	110.00
83/11/25	1620	116.00	0.00	5.15	14.30	850.00	30.00	90.00
83/11/25	1627	90.00	0.00	5.15	14.40	800.00	30.00	80.00

Phox System Data

Date	Time	Flow	DO	pH	Temperature	Chloride	Conductivity	Turbidity
83/11/25	1651	95.00	0.00	5.20	14.60	750.00	30.00	50.00
83/11/25	1658	100.00	0.00	5.20	14.80	760.00	30.00	50.00
83/11/25	1704	95.00	0.00	5.20	14.90	760.00	30.00	50.00
83/11/25	1710	120.00	0.00	5.20	15.00	750.00	30.00	30.00
83/11/25	1717	191.25	0.00	5.15	14.80	760.00	30.00	50.00
83/11/25	1723	195.31	0.00	5.15	15.00	760.00	30.00	75.00
83/11/25	1729	250.00	0.00	5.15	15.40	760.00	30.00	100.00
83/11/25	1736	400.00	0.00	5.15	15.50	780.00	30.00	75.00
83/11/25	1742	400.00	0.00	5.10	15.20	780.00	30.00	50.00
83/11/25	1748	446.88	0.00	5.10	15.40	780.00	30.00	25.00
83/11/25	1754	400.00	0.00	5.10	15.00	800.00	30.00	20.00
83/11/25	1801	350.00	0.00	5.10	15.00	780.00	30.00	15.00
83/11/25	1807	250.00	0.00	5.10	15.00	770.00	30.00	15.00
83/12/17	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
83/12/17	454	90.00	9.00	7.30	9.75	0.00	280.00	900.00
83/12/17	457	90.00	9.40	7.50	9.80	0.00	260.00	1000.00
83/12/17	501	85.00	9.60	7.60	9.90	0.00	258.00	900.00
83/12/17	504	80.00	9.60	7.60	9.95	0.00	260.00	950.00
83/12/17	507	77.34	9.60	7.60	10.00	0.00	270.00	850.00
83/12/17	510	75.63	9.60	7.60	10.00	0.00	275.00	800.00
83/12/17	513	74.84	9.60	7.60	10.00	0.00	285.00	800.00
83/12/17	1101	255.47	10.20	7.50	9.75	0.00	110.00	720.00
83/12/17	1104	333.59	10.40	7.60	9.40	0.00	80.00	710.00
83/12/17	1107	378.32	10.50	7.60	9.10	0.00	70.00	700.00
83/12/17	1110	385.16	10.50	7.50	9.00	0.00	70.00	690.00
83/12/17	1113	385.16	10.75	7.45	9.00	0.00	80.00	680.00
83/12/17	1117	371.88	10.80	7.45	9.25	0.00	90.00	640.00
83/12/17	1120	354.88	10.80	7.50	9.25	0.00	80.00	620.00
84/01/02	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
84/01/02	1324	105.00	8.40	6.40	9.00	0.00	80.00	1110.00
84/01/02	1330	110.00	9.40	7.10	9.25	0.00	80.00	1110.00
84/01/02	1336	115.00	9.50	7.40	9.50	0.00	80.00	1110.00
84/01/02	1343	110.00	9.50	7.50	9.50	0.00	71.00	1100.00
84/01/02	1349	100.00	9.50	7.50	9.00	0.00	69.00	1090.00
84/01/02	1355	120.00	9.50	7.90	9.00	0.00	60.00	1050.00
84/01/02	1401	130.63	9.50	7.50	9.00	0.00	60.00	1035.00
84/01/02	1408	140.00	9.50	7.40	9.40	0.00	60.00	1000.00
84/01/02	1414	149.84	9.50	7.40	9.00	0.00	58.00	970.00
84/01/02	1420	191.25	9.50	7.40	9.40	0.00	50.00	920.00
84/01/02	1426	218.75	9.50	7.30	9.25	0.00	45.00	900.00
84/01/02	1433	231.25	9.60	7.30	9.40	0.00	40.00	890.00
84/01/02	1439	243.75	9.70	7.30	9.25	0.00	40.00	890.00
84/01/02	1445	250.00	9.70	7.30	9.40	0.00	40.00	875.00
84/01/02	1452	255.47	9.50	7.30	9.75	0.00	40.00	825.00
84/01/02	1458	261.46	9.50	7.30	9.75	0.00	38.00	600.00
84/01/02	1504	261.46	9.60	7.25	9.75	0.00	30.00	560.00
84/01/02	1510	237.50	9.50	7.20	9.50	0.00	30.00	550.00
84/01/02	1517	206.25	9.50	7.20	9.80	0.00	30.00	545.00
84/01/02	1523	191.25	9.40	7.20	9.90	0.00	30.00	520.00
84/01/02	1529	187.81	9.50	7.20	9.80	0.00	30.00	500.00
84/01/02	1535	191.25	9.50	7.20	10.00	0.00	30.00	450.00
84/01/02	1542	225.00	9.40	7.20	10.00	0.00	30.00	445.00
84/01/02	1548	250.00	9.40	7.20	10.00	0.00	30.00	440.00

Phox System Data

Date	Time	Flow	DO	pH	Temperature	Chloride	Conductivity	Turbidity
84/01/22	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
84/01/22	1259	90.00	0.40	6.00	8.50	0.00	15.00	150.00
84/01/22	1305	90.00	3.40	6.10	7.50	0.00	15.00	120.00
84/01/22	1311	95.00	6.20	6.20	9.00	0.00	30.00	110.00
84/01/22	1318	100.00	7.00	6.30	9.00	0.00	100.00	100.00
84/01/22	1324	102.50	6.60	6.40	10.40	0.00	210.00	90.00
84/01/22	1330	105.00	6.40	6.60	10.90	0.00	230.00	85.00
84/01/22	1336	110.00	6.00	6.60	11.40	0.00	230.00	90.00
84/01/22	1342	110.00	5.80	6.70	12.00	0.00	230.00	90.00
84/01/22	1348	120.00	6.00	6.70	12.00	0.00	230.00	90.00
84/01/22	1355	120.00	5.60	6.80	12.60	0.00	220.00	98.00
84/01/22	1401	130.63	5.80	6.80	13.10	0.00	220.00	100.00
84/01/22	1407	135.47	5.40	6.80	13.50	0.00	210.00	100.00
84/01/22	1413	135.47	5.20	6.85	13.60	0.00	210.00	100.00
84/01/22	1419	135.47	5.40	6.85	14.00	0.00	200.00	100.00
84/01/22	1426	140.00	5.00	6.85	14.00	0.00	200.00	100.00
84/01/22	1432	140.00	4.60	6.90	13.50	0.00	190.00	100.00
84/01/22	1438	140.00	4.40	6.90	14.40	0.00	185.00	100.00
84/01/22	1444	140.00	4.20	6.90	14.30	0.00	180.00	99.00
84/01/22	1450	135.47	4.00	6.90	14.30	0.00	175.00	98.00
84/01/22	1457	135.47	3.80	6.85	14.50	0.00	175.00	97.00
84/01/22	1503	135.47	3.60	6.85	14.50	0.00	175.00	95.00
84/01/22	1509	130.63	3.50	6.85	14.40	0.00	175.00	90.00
84/01/22	1515	130.63	3.50	6.85	14.40	0.00	160.00	90.00
84/01/22	1521	120.00	3.60	6.85	14.40	0.00	150.00	90.00
84/05/10	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
84/05/10	1733	0.00	7.00	7.60	11.75	0.00	270.00	340.00
84/05/10	1737	0.00	8.00	7.50	12.00	0.00	245.00	350.00
84/05/10	1742	0.00	7.70	7.30	12.00	0.00	240.00	350.00
84/05/10	1746	0.00	7.90	7.30	12.00	0.00	240.00	330.00
84/05/10	1750	0.00	7.60	7.30	11.25	0.00	220.00	320.00
84/05/10	1754	0.00	7.30	7.40	12.00	0.00	220.00	320.00
84/05/10	1758	0.00	7.00	7.40	11.50	0.00	230.00	320.00
84/05/10	1802	0.00	6.50	7.40	12.20	0.00	230.00	310.00
84/05/10	1806	0.00	6.50	7.30	12.20	0.00	230.00	310.00
84/05/10	1810	0.00	6.30	7.30	12.20	0.00	230.00	300.00
84/05/10	1814	0.00	6.00	7.30	12.20	0.00	230.00	300.00
84/05/10	1818	0.00	5.60	7.30	12.20	0.00	230.00	300.00
84/05/10	1822	0.00	5.20	7.30	12.25	0.00	230.00	300.00
84/05/10	1826	0.00	5.00	7.30	12.25	0.00	230.00	290.00
84/05/10	1830	0.00	4.60	7.30	12.25	0.00	235.00	290.00
84/05/10	1834	0.00	4.40	7.30	12.25	0.00	235.00	280.00
84/05/10	1838	0.00	4.20	7.30	12.25	0.00	235.00	275.00
84/05/10	1842	0.00	4.00	7.30	12.25	0.00	235.00	275.00
84/05/10	1846	0.00	4.00	7.30	12.40	0.00	230.00	260.00
84/05/10	1848	0.00	3.90	7.30	12.40	0.00	230.00	250.00
84/05/24	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
84/05/24	1540	2012.54	6.70	7.00	16.75	0.00	240.00	1110.00
84/05/24	1548	1550.00	6.70	7.00	19.20	0.00	215.00	850.00
84/05/24	1556	1300.00	6.40	7.00	19.20	0.00	220.00	700.00
84/05/24	1605	586.25	5.50	7.00	19.40	0.00	220.00	600.00
84/05/24	1613	400.00	4.40	7.00	19.50	0.00	220.00	520.00
84/05/24	1621	191.25	4.00	7.00	19.70	0.00	220.00	450.00

Phox System Data

Date	Time	Flow	DO	pH	Temperature	Chloride	Conductivity	Turbidity
84/05/24	1629	110.00	4.00	7.00	20.20	0.00	220.00	400.00
84/05/24	1638	446.88	3.60	6.90	20.50	0.00	220.00	380.00
84/05/24	1646	365.82	3.50	6.90	20.60	0.00	220.00	370.00
84/05/24	1654	250.00	3.00	6.90	20.75	0.00	220.00	350.00
84/05/24	1703	163.91	2.90	6.90	20.75	0.00	220.00	340.00
84/05/24	1711	110.00	2.80	6.90	21.00	0.00	220.00	330.00
84/05/25	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
84/05/25	2233	120.00	0.00	6.90	11.50	0.00	240.00	240.00
84/05/25	2237	125.47	0.25	6.90	11.50	0.00	240.00	220.00
84/05/25	2245	135.47	5.50	6.90	11.10	0.00	255.00	200.00
84/05/25	2253	140.00	6.20	6.80	10.50	0.00	260.00	180.00
84/05/25	2301	142.34	6.00	6.80	11.50	0.00	260.00	175.00
84/05/25	2309	191.25	5.80	6.80	11.50	0.00	260.00	170.00
84/05/25	2317	261.46	5.70	6.80	12.30	0.00	260.00	180.00
84/05/25	2325	250.00	5.60	6.80	12.40	0.00	250.00	185.00
84/05/25	2334	205.25	5.60	6.80	12.00	0.00	245.00	185.00
84/05/25	2342	155.00	5.50	6.80	11.50	0.00	240.00	190.00
84/05/25	2350	120.00	4.50	6.80	13.00	0.00	240.00	190.00
84/06/20	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
84/06/20	50	90.00	1.00	5.10	23.00	0.00	260.00	0.00
84/06/20	54	195.31	3.50	5.60	22.50	0.00	450.00	0.00
84/06/20	1612	140.00	3.60	5.30	25.50	840.00	0.00	300.00
84/06/20	1617	77.34	5.60	6.00	21.50	0.00	240.00	290.00
84/06/20	1621	120.00	5.50	6.30	21.25	0.00	240.00	260.00
84/06/20	1628	90.00	4.80	6.70	21.25	0.00	240.00	240.00
84/06/20	1632	74.84	5.20	6.80	20.25	0.00	240.00	170.00
84/06/20	1827	558.83	1.80	6.80	21.50	0.00	245.00	130.00
84/06/20	1831	465.63	5.40	6.80	21.00	0.00	225.00	140.00
84/06/20	1835	365.82	6.00	6.80	20.60	0.00	220.00	140.00
84/06/20	1839	306.05	6.00	6.80	20.50	0.00	220.00	145.00
84/06/20	1843	237.50	6.00	6.90	20.20	0.00	220.00	145.00
84/06/20	1848	171.88	8.40	6.80	18.50	0.00	260.00	0.00
84/06/20	1852	120.00	8.40	6.90	18.50	0.00	255.00	0.00
84/06/20	1855	100.00	8.40	6.90	18.50	0.00	260.00	0.00

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