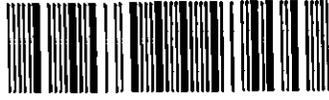


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METAL SPECIATION IN URBAN RUNOFF

by

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## METAL SPECIATION IN URBAN RUNOFF

G. M. MORRISON

### ABSTRACT

A literature review has identified free and weakly complexed dissolved, as well as solid surface associated, metal species as those forms most likely to be bioavailable. To analyse bioavailable Zn, Cd, Pb and Cu fractions in urban runoff a speciation scheme was devised which provided a relatively rapid technique for separating the dissolved and suspended solid phases of stormwater into appropriate fractions.

A new method, termed *Dialysis with Receiving Resins*, which responds to bioavailable metal species by incorporating a specially developed cysteine resin, within a dialysis membrane, has been devised and tested.

A small scale gullypot study allowed the identification of six major processes which affect metal mobilisation and transport. The relevance of these processes is discussed with reference to gullypot outflow loadings of the different metal fractions. Acid rain mobilisation was found to greatly increase the levels of bioavailable free and weakly complexed metal fractions. Mass balance studies showed that Zn, Cd and Cu have a residence time in the road surface/gullypot system of little more than one storm event whereas Pb tends to be more persistent due to its predominant association with the solid phase.

The speciation scheme was also applied to the analysis of metal fractions in stormwater outfall samples collected from urban catchments in Sweden and the U.K. Significant concentrations and loadings of metals were found for both catchments with, on average, bioavailable metal forms representing 68% of the Zn, 76% of the Cd, 66% of the Pb and 32% of the Cu. Individual metal species were found to load at different rates onto metal chemographs and can be explained in terms of controlling parameters, as well as the influence of mobilisation and transport processes.

Cadmium and Cu concentrations in stormwater were regularly found to exceed Water Quality Standards and also to accumulate to significant levels in the *Dialysis with Receiving Resins* method. These metals may therefore represent a direct threat to receiving water quality.

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## CHAPTER 1 INTRODUCTION.

This thesis considers the findings from a co-operative three year project, conducted during the period 1982-1985, between the Urban Pollution Research Centre, Middlesex Polytechnic, U.K. and the Department of Sanitary Engineering, Chalmers University of Technology, Sweden.

### 1.1 Stormwater Pollution Research at Middlesex Polytechnic and Chalmers University of Technology.

The interest in stormwater runoff as a potential source of receiving water pollution, both in Sweden and the U.K., can be traced back to the 1950's (e.g. Wilkinson 1956). The rapid construction of urban overspill developments in the 1960's further concentrated attention upon this potential pollution problem to receiving waters.

Combined sewer systems were built within many post-war housing developments, although many smaller, residential overspill areas (< 350 ha) were developed using a separate sewer system design. These systems discharge impermeable surface runoff directly and without treatment to the nearest watercourse. The cost of the doubling of sewer construction in separate systems was considered to be offset by the long term economy of stabilised and reduced wastewater flows to the sewage treatment plants. Any detrimental environmental costs for the receiving water bodies from stormwater and combined sewer overflow effluents were clearly not of prime concern. Most authorities regarded the receiving body as providing sufficient dilution capacity to safeguard the quality and long term standards of the receiving waters.

Distinct and specific areas of concern were raised, in the early 1970's, about the situation in both Sweden (Malmqvist 1983) and the U.K. (Ellis 1976). It was emphasised that little was known about the origins, transport and transformations of priority pollutants through the stormwater system, both in terms of immediate and delayed effects.

It was also questioned whether separately sewered stormwater outflow priority pollutant concentrations were in exceedance of those from treated effluent discharges and sewer overflow effluents. Without any basic information on these issues no reliable predictions concerning the impact of stormwater discharges could be made.

Early research by the Department of Sanitary Engineering, Chalmers University of Technology, Gothenburg, Sweden (Lisper 1974) showed that runoff from highway surfaces was capable of scavenging significant quantities of priority pollutants, particularly oxygen demanding organics and heavy metals. Consequently, a working group was set up in the Department of Sanitary Engineering and a preliminary investigation, within the Bergsjön catchment in Gothenburg, revealed that heavy metals were present in significant concentrations both in rainfall and stormwater (Horkeby and Malmqvist 1977). The results of this early study are summarised in Table 1.1 and show that atmospheric fallout can clearly contribute significant amounts of metals to the total stormwater load. Seasonal concentration differences were also apparent, although only one sample was taken for each season. To verify and expand upon this early data a project, commencing in 1975, was established to analyse priority pollutants within four residential catchments for a representative number of storm events.

In 1975 the regular monitoring of priority pollutants in stormwater samples from the Grahame Park catchment, Hendon, London, was commenced and this led to the establishment of the Urban Pollution Research Centre at Middlesex Polytechnic in late 1976. Significant loadings of organic compounds, nutrients, faecal bacteria, heavy metals and suspended solids were observed in stormwater discharges from the Grahame Park 353 ha. separately sewered residential catchment (Ellis 1975, 1976). Accumulated benthal sludge in the receiving stream was found to exert a large oxygen demand and a significant potential source of heavy metals.

Table 1.1 Metal Levels for Stormwater and Atmospheric Fallout at Bergsjön, Gothenburg.

	Atmospheric Fallout µg/l			Stormwater µg/l		
	Spring	Summer	Autumn	Spring	Summer	Autumn
Zinc	95	52	127	243	335	685
Cadmium	1.0	-	4.3	1.0	5.2	12.1
Lead	60	96	90	350	140	24
Copper	18	4	30	174	215	215

The flux of suspended solids did not always pass through the storm drainage system as a single "first flush" pulse consonant with peak flow; two peaks of solids being commonly observed. The first peak, preceding or coincident with peak flow, was related to the remobilisation of settled deposits from the previous storm event. The second solids peak, coming after peak flow, was related to the introduction of fresh sediment from road surface drainage (Ellis 1976).

The results of work from both groups was presented at a UNESCO symposium in Amsterdam (Effects of Urbanization and Industrialization on the Hydrological Regime and on Water Quality) and the first contact between the Swedish and U.K. groups was made. The U.K. group reported that the regular monitoring of the Grahame Park catchment had allowed the "first flush" of polluted material, when it occurred, to be primarily related to the concentration time for the catchment. Fine solids were identified as an important pollution source and, although only 4-8% of road solids were composed of particles finer than 60 µm,

this fraction accounted for 25% of oxygen demand, 30-50% of nutrients, 30% of heavy metals and 10% of the bacteria (Ellis 1977).

At the same symposium the Swedish group showed that stormwater heavy metal sources were predominantly a result of atmospheric fallout, building material corrosion and traffic (Malmqvist and Svensson 1977). As part of the Swedish research project a continuous monitoring station was set up at the Bergsjön stormwater outfall in Gothenburg and this site has been continually improved. The unique ten year data record obtained from the sampling station includes continuous storm and baseflow monitoring of pH, turbidity, temperature, flow and conductivity (Morrison et al. 1985).

Research on stormwater pollutant release patterns continued at both the Swedish and U.K. catchments, with an increasing emphasis on the biogeochemical interactions and transport of pollutants through the stormwater system. Data from the Bergsjön catchment, as well as other Swedish residential urban catchments have provided the range of average metal concentrations shown in Table 1.2. These results were found to be useful in providing guidelines for the heavy metal concentrations to be expected in stormwater runoff, particularly for the engineering design of new Swedish urban areas (Malmqvist 1983).

Table 1.2 Precipitation and Urban Runoff Heavy Metal Concentrations in Sweden (from Malmqvist 1983).

	Precipitation µg/l	Urban Runoff µg/l
Zinc	25	60-920
Lead	20-80	50-460
Copper	5	18-330

The pathways of heavy metals through the stormwater system were investigated by a mass balance approach for four Swedish urban residential catchments (Malmqvist 1983). The results in respect of Cu and Pb are discussed below for the 15.6 ha Bergsjön catchment. For Pb, some 40 Kg/year enters the catchment from traffic sources, with 6.9 Kg/year contributed from atmospheric fallout. Of this input only 3.8 Kg/year leaves the catchment as stormwater runoff. Accumulation on the permeable surfaces appears to account for the difference. However, the variable release of low Pb concentrations into baseflow from in-pipe sediments may have been under-estimated by the sampling procedure. In contrast, Cu within the Bergsjön catchment is dominated by atmospheric fallout (3.12 Kg/year) and corrosion of construction surfaces (2.71 Kg/year), while only a small amount is contributed by traffic sources (0.07 Kg/year). However, a large amount is removed in stormwater runoff (3.93 Kg/year) which may be explained by the direct entry of roof runoff into the storm sewer system.

The U.K. research group compiled the data published prior to 1981 and included soluble stormwater metal concentrations, which are more relevant than total metal concentrations to receiving water body toxicity (Ellis and Revitt 1982). The values, shown in Table 1.3, are for residential catchments only. Clearly Pb, despite high road sediment and total stormwater concentrations, does not compare in solubility to the other metals. Total metal concentration might not therefore provide the best indication of toxicity to receiving water biota. This is of particular importance as stormwater may contribute 50-70% of the total heavy metal loadings to receiving waters (Colwill et al. 1984).

Table 1.3 Metal Concentration Ranges in Road Sediment and Stormwater (from Ellis and Revitt 1982).

	Road Sediment	Stormwater	Soluble Phase of Stormwater
	µg/g	µg/l	µg/l
Zinc	13-1110	8-4600	<15-1200
Cadmium	0.0034-10.1	0.8-8.0	<0.5-5.0
Lead	128-8300	250-26000	10-180
Copper	25-3170	7-1410	4-200

To assess metal solubility Revitt and Ellis (1980) carried out leachate studies on road dusts using collected rainfall. Cadmium was found to be extracted 1000 times more readily than Pb, although Zn showed the highest overall leachate levels. Another method of assessing the availability of metals to the soluble phase is through road dust speciation analysis, and one such study provided an overall availability order of Cd > Zn > Pb > Cu (Hamilton et al 1984).

An enrichment of solid associated metal through the drainage system also appears to occur. Harrop et al. (1983) found that metals were enriched between two and four times in sediments removed to gullypots compared to those of road surface dusts. Metals tend to show a log normal distribution with respect to particle size on the road surface. Therefore the enriched metal levels found within the stormwater system can at least partly be explained by the preferential washoff of more toxic fines from the road surface (Revitt et al. 1981, Harrop et al. 1983). However, atmospheric derived particles also need to be taken into account and Hamilton and Adie (1982) reported that urban aerosols contain average Pb concentrations of 10000 µg/g.

With the exception of suspended solids, most pollutants discharged from a small, well defined 0.5 ha. highway catchment in Oxhey, Hertfordshire (N.W. London), demonstrate a distinct tendency towards a "first flush" (Harrop 1984). This tendency is replicated in the Bergsjön catchment where only 54% of 190 storm events in 1983/1984 showed a "first flush" as demonstrated by turbidity recordings (Morrison et al 1985). Correspondingly, suspended solid associated metals were generally found to have discharged only 20-30% of the total storm metal within the time of concentration for the Grahame Park catchment, U.K. (Revitt et al. 1981).

A fingerprinting of metal transport from different sources through the stormwater system has been obtained by defining the distinctive magnetic properties of atmospheric fallout and automobile emissions (Revitt et al. 1981). This method forms the basis of an ongoing project within the Urban Pollution Research Centre (Beckwith et al. 1984)

The biological uptake of metals by receiving water organisms is currently under investigation within the U.K. catchment (Ellis et al. 1985). It may be that certain organisms can survive near storm drainage outfalls due to their capability of producing metal-binding proteins, which act as a metal detoxification mechanism.

The convergence of interest between the Swedish and English groups became focused in 1982, following the allocation of a Natural Environment Research Council CASE award to the Urban Pollution Research Centre, Middlesex Polytechnic, in collaboration with the Urban Geohydrology Group, Chalmers University of Technology, to study *Metal Speciation in Urban Runoff*.

After an early meeting between both groups in Gothenburg in November 1982, the project was planned and a further successful grant application, this time to the Swedish National Environment Protection Board, resulted in sufficient financial support for a three year project to be undertaken.

To maintain the co-operation regular contact between both groups was continued with meetings in either England or Sweden in July 1983, November 1983, June 1984 and March 1985. Although the immediate aim of the project was the production of this thesis, six international journal and conference proceedings publications, as well as one internal report, were also produced during the period 1982-1985.

The collaboration between the Swedish and English groups is to continue in 1986 with studies on the biological and chemical fate of metal species in the receiving waters of stormwater discharges.

### 1.2 Aims and Objectives of the Research Project.

The aim of the research project was to identify the physico-chemical forms of Cd, Cu, Pb and Zn and their temporal patterns of discharge from separately sewered catchments characteristic of European urban development. This would provide information relating to their transport through the stormwater system and a guide to their potential toxic effects on receiving waters. With these criteria in mind the following objectives were set.

- a) To test and develop physico-chemical methods for the determination of bioavailable metal species in stormwater.
- b) To incorporate these physico-chemical methods into a speciation scheme which allows the relatively rapid determination of Zn, Cd, Pb and Cu species in urban runoff and provides information on the bioavailability and geochemical mobility of the metals.
- c) To determine temporal patterns and forms of metal species in the runoff from urban catchments.
- d) To interpret the different metal forms in storm profiles with respect to changes in hydrological, physical and chemical parameters, as well as their relationship to catchment characteristics and climatic and seasonal variables.
- e) To identify the important physical and chemical processes affecting metal speciation by analysing speciation changes through a relatively simple gullypot system.

### 1.3 Outline of Thesis.

A review of previous work on metal speciation in natural waters and biological toxicity studies is reported in Chapter 2, together with reported concentrations and loadings of metals in urban runoff. Previously used metal speciation techniques, for both the dissolved and suspended solid phases are discussed and related to the possibility of identifying bioavailable metal species in stormwater. To supplement this central theme, theoretical metal speciation studies and the role of metal complexing organic ligands are discussed. The importance of proper sampling and clean analytical methods are also considered.

In order to provide a suitable data base it was necessary to develop and maintain catchment instrumentation. The stormwater outfall sampling stations at Oxhey (U.K.) and Bergsjön (Sweden) are described in Chapter 3. Details are also given for the gullypot sampling and continuous monitoring facilities installed for this project on the Chalmers catchment (Sweden).

The laboratory development of, and preliminary work on, the metal speciation scheme for the analysis of the collected stormwater samples is described in Chapter 4. Further speciation studies, including an attempt to simulate biological metal uptake by developing a new method termed *Dialysis with Receiving Resins*, are described in Chapter 5.

The metal speciation results for six storms, collected in the summer of 1984, from the Chalmers gullypot catchment, are considered in Chapter 6. Metal species transport mechanisms, gullypot outflow loadings and mass balances, for individual storm events, are discussed.

In Chapter 7 metal speciation results are presented, for ten urban runoff events (rainfall and snowmelt initiated) from the Oxhey (U.K.) and Bergsjön (Sweden) catchments. The variations of metal species loadings through individual storm events are discussed in terms of

source input contributions. The potential effects on receiving waters of stormwater derived metals are predicted by adopting both the Water Quality Standard and *Dialysis with Receiving Resins* approaches.

In the final Chapter the main findings are summarised and are discussed in terms of the implications for municipal road and sewer cleaning practices and receiving stream impacts. Future research strategies in the field of urban runoff metal pollution are proposed based on the major results obtained in this project.

## CHAPTER 2 HYDROCHEMICAL ASPECTS OF METAL SPECIATION: A REVIEW.

### 2.1 Heavy Metals in the Urban Environment and their Potential Toxicity in Storm Runoff.

Heavy metal loadings, which originate from the urban environment, may represent a significant amount of the total metal entering local receiving waters (Ellis et al. 1985, Oberts 1985, Perry and McIntyre 1985). Stormwater runoff washes metals from impermeable surfaces and, in separately sewered areas, discharges them directly into a stream or lake. Comparisons with water quality standards will demonstrate that these intermittent heavy metal discharges may exceed defined chronic and acute biotic criteria.

#### 2.1.1 Heavy Metals in Urban Surface Runoff.

Urban surface runoff may include any natural or pollutant material that is available for transport within the catchment area. Increased urban surface impermeability results in both increased runoff and heavy metal loadings (Lindholm and Balmér 1978, Oberts 1985). The degree of industrialisation, traffic type and volume and road surface condition within the urban catchment will also affect heavy metal contributions. There is a considerable variation and inconsistency in the reported concentrations of heavy metals in storm runoff discharges (Ellis 1982, Harrop 1984, Oberts 1985). Variations in metal loadings over individual storm hydrographs may be explained by a Variable Contributing Area Concept (Morrison et al. 1984a), Kinematic Wave Theory and Dilution-Exhaustion effects (Ellis 1982).

In spite of the potential number of contributing sources within the urban catchment three main inputs can be identified and are discussed below.

#### 2.1.1.1 Wet and Dry Atmospheric Deposition.

Significant quantities of heavy metals have been reported in urban precipitation (Cawse 1974, Malmqvist and Svensson 1977, Malmqvist 1983). It has been shown that, even in relatively unpolluted areas, rainfall and dry dustfall may be an important contributing source of heavy metals in stormwater runoff (Randall et al. 1978).

As a typical example Owe et al. (1982) have reported precipitation and runoff heavy metal levels for a parking lot (Table 2.1) and clearly precipitation provides a background concentration of metals which is greatly increased after washoff from the urban surface. In terms of loadings, precipitation derived Pb represented 16% of the total Pb discharged in runoff from the catchment.

Table 2.1 Metal Concentrations in Precipitation and Parking Lot Runoff (from Owe et al. 1982).

	Precipitation µg/l	Parking Lot Runoff µg/l
Zinc	47-166	890-4740
Cadmium	1-4	10-280
Lead	58-186	730-2970
Copper	5-95	120-1380

The separation of dry aerial dustfall from wind blown dust, as well as from wet deposition, represents a difficult sampling problem.

### 2.1.1.2 Urban Surfaces.

The urban surface is a non-point source which provides an important contribution of heavy metals to urban runoff. Automobiles have been conclusively identified as one of the major sources of impermeable surface input (Bryan 1974, Newton et al. 1974). Christensen and Guinn (1979) reported the average deposition rates of metals on road surfaces to be 0.003 g Zn/vehicle km and 0.0049 g Pb/vehicle km. The major sources of heavy metals found on urban surfaces, together with particulate metal concentrations, are given in Table 2.2. Corrosion of, and emissions from, automobiles obviously represents a very significant metal contribution. The rate of metal build-up on the road surface should be related to traffic density and type, duration of the dry period and removal processes, as well as the season of the year (Owe et al. 1982).

Table 2.2 Sources of Heavy Metals found on Urban Surfaces (from Shaheen 1975, Atkins and Hawley 1978, Brinkmann 1984, Cole et al 1984, Wilson 1984, Beckwith et al. 1985).

Metal	Sources	Concentration $\mu\text{g/g}$
Zinc	Automobile Tyres	630
	Motor Oils	12-1060
	Automatic Transmission Fluids	-
	Car Brake Linings	124-22500
	Gasoline	10
	Car Exhaust Particulates	8105-186612
	Car Corroded Bodywork	108-6611

contd.

Metal	Sources	Concentration $\mu\text{g/g}$
Zinc	Rust Inhibitor and Antifreeze	-
	Road Salt	-
	Road Pavement	12-267
	Building Materials/Urban Structures	-
	Paints	-
	Wood Preservative	-
	Water Treatment Chemicals	-
	Pesticides and Biocides	-
Cadmium	Car Tyres	1
	Motor Oils	0.2-0.26
	Car Corroded Bodywork	0.2
	Car Brake Linings	0-5
	Car Battery	-
	Car Exhaust Particulates	4.8-5.6
	Road Pavement	0-1
	Alloys and Plated Surfaces	-
	Wood and Canvas Preservative	-
	Water Treatment Chemicals	-
	Pesticides	-
Lead	Petrol Additives	150
	Car Exhaust Particulates	1192-119420
	Car Corroded Bodywork	32-116
	Motor Oils	9-12
	Car Tyres	1000
	Car Brake Linings	1050-35000
	Traffic Paint	-

contd.

Metal	Sources	Concentration $\mu\text{g/g}$
Lead	Anti-corrosion Paint	-
	Road Pavement	0.7-122
	Pesticides	-
Copper	Petrol Additives	4
	Motor Oils	3-8
	Car Exhaust Particulates	58-68
	Car Brake Linings	14476-200000
	Corroded Bodywork	55
	Tyres	252
	Road Pavement	51-73.6
	Building Materials	-
	Anti-algal Paints	-
	Algicides	-
	Wood and Canvas Preservatives	-
	Water Treatment Chemicals	-

Another potential major input of metals from urban surfaces is that derived from roof and gutter construction materials. In Scandinavia, Cu is commonly used for roof gutters and in some cases even the roof itself. The subsequent corrosion of this material may generate large amounts of Cu and deliver it to the sub-surface system (Malmqvist and Svensson 1977). Zinc is commonly used for street furniture and lampposts, in both the U.K. and Sweden, which can likewise be corroded.

In addition to this knowledge of the dominant metal sources there is an obvious need to identify the physical and chemical processes affecting metal mobilisation into the below ground system during storm events.

### 2.1.1.3 Sub-surface Deposition.

This category includes in-pipe deposition and gullypot accumulations. Metal concentrations in sediments (>1000  $\mu\text{m}$ ) found in gullypots and in-pipe are compared with surface sediments for a small highway catchment in Table 2.3. The heavy metal concentrations are higher on the street surface and in the below ground system than in the roof sediments (Beckwith et al. 1985). Zinc, Pb and Cu clearly can be traced to car derivatives deposited on the road surface. However, Cd shows an anomalous concentration in pavement sediment which is difficult to explain. The below ground sediments may represent a mixture of these sources and certainly the concentrations in Table 2.3 can be interpreted as reflecting such a process.

Table 2.3 Mean Sediment Metal Concentrations for different Sources to the Stormwater Sewer (from Beckwith et al. 1985).

	Mean Sediment Metal Concentration $\mu\text{g/g}$			
	Zinc	Cadmium	Lead	Copper
Pavement	186.1	2.2	134.0	40.4
Road Gutter	292.6	0.7	452.1	50.6
Road Centre	499.8	0.4	1041.1	87.8
Roof Surface	375.8	1.3	419.4	30.3
Roof Gutter	289.3	0.7	418.7	26.8
Gullypot	490.4	2.0	608.1	67.4
In-pipe	415.4	1.5	472.2	50.5

Gullypot and in-pipe sediments may be the first solids washed out during a storm event. However, most of this sediment will lag as saltatory particles (Ellis 1976) so that only the fine heavy metal

enriched particles are found as suspended solids at the stormwater outfall.

The gullypot sediment may undergo chemical changes during dry periods, particularly as several workers have observed evidence of anoxic conditions (Mance and Harman 1978, Fletcher and Pratt 1981, Harrop 1984). During the first anoxic stages of gullypot sediment maturation, i.e. nitrate reduction, the increased ammonia and dissolved organic carbon levels might be expected to result in a build-up of the soluble "bound" species of Cu and Pb in the anoxic interstitial water (Forstner and Salamons 1983). As the anoxic conditions continue sulphide, from protein catabolism, can act as an important precipitating agent for metals (Forday and Greenfield 1983). Insoluble metal sulphide forms are more strongly sediment bound than surface associated carbonate and hydrous Fe and Mn oxide species (Luoma and Bryan 1981).

Oxic/anoxic sediment maturation may alter the transport mechanisms and dissolved/particulate phase distributions of heavy metals in stormwater passing through the gullypot and in-pipe system, but the extent to which this occurs is not known.

#### 2.1.2 Variations of Heavy Metal Loadings during Storm Events.

The complexity of contributing area and below ground physical mobilisation processes has not allowed a full understanding of how urban heavy metal source loadings are reflected in the stormwater discharges at the outfall of the catchment pipe system.

Certainly a "first flush" of highly turbid water, lasting for some 20 to 30 minutes, has been observed at the beginning of storm events (Wilkinson 1956). In some storm events a "first flush" is not observed for suspended solids; and in addition secondary and multiple peaks have been found (Harrop 1984). Ellis (1982) has discussed the importance of the time of concentration for the catchment which can explain the lack of "first flush" noted in some storm events. It can

be argued that the "first flush" is a combination of gullypot and in-pipe sediment washoff (Ellis 1982). The energy for road surface sediment washoff is created by the processes of surface wetting, rainfall intensity and water flow. Gullypot and in-pipe physical mobilisation should be mainly dependent on water flow energy (Morrison et al. 1985).

From these observations heavy metal loadings might be expected to be concentrated in the first part of the storm event (Mance 1981). This assertion is based on the strong affinity of metals for stormwater suspended solids (Bourcier and Sharma 1980, Urbonas and Tucker 1980, Wilber and Hunter 1980), which often parallel the storm hydrograph. However, direct measurements through individual storms have not shown a metal "first flush", except in the case of Cd for one storm event (Revitt et al 1981).

This apparent discrepancy in views might suggest that metal inputs are being delivered from a variety of sources, in addition to being physically and chemically mobilised at different rates, and are thus loaded onto the hydrograph at different times. Size sorting during physical sediment mobilisation, as well as chemical changes at the solid surface during stormwater transport, can also affect the discharged metal levels (Morrison et al. 1984b).

It is known that stormwater solids are enriched with metals. Wilber and Hunter (1979) found that urban discharges resulted in the following metal enrichments, for stream sediments below stormwater effluent inputs, over those sediments upstream; Pb x6.7, Cu x3.1, Cd x5.2, Zn x3.5. Chemical fractionation of the stormwater solids (Wilber and Hunter 1979) revealed that about 10% of the Cu and 20% of the Zn and Pb was in a readily chemically mobilised form.

Many of the heavy metal studies which have been carried out do not differentiate between particulate and dissolved metals, or alternatively measure only the particulate associated metal. When relating metal levels to toxic effects it is important to recognise

that there is often a considerable loading of dissolved metal in storm discharges. In addition, metals may be mobilised from the particulate phase to the dissolved phase and Cd, in particular, has been shown to be readily solubilised from road sediments (Revitt and Ellis 1980). Thus a knowledge of heavy metal kinetics and speciation is important if advances are to be made in evaluating the relative toxicity of urban non-point discharges.

### 2.1.3 The Toxicity of Heavy Metals to Aquatic Life.

In order to determine the toxic or bioavailable fractions of heavy metals, a basic understanding of their effects on aquatic life is required. The actual toxicity of a metal to a particular organism will depend on many factors such as age, surface area, population structure and competing metal ion concentrations.

Certain processes at the organism/environmental interface also affect metal uptake (Luoma 1983). These include;

- a) the interface characteristics
- b) the reactivity of the metal form with the interface
- c) antagonism or metal uptake stimulation by other metals or major cations
- d) temperature

However, some specific heavy metal forms are potentially more toxic and are likely to be hazardous to the biota of a receiving water. Generally non-essential elements, such as Pb and Cd, are usually more toxic than essential elements, such as Zn and Cu, although an excess of either may be detrimental (Batley 1983).

Initial heavy metal toxicant studies have been concerned with the relationship between total metal concentrations and their toxicity to organisms. However, recent research points to the free and weakly complexed ions as being the toxic forms of the metal (Stumm 1983). This has been experimentally verified through the observation of the interactions between the chemical form of a heavy metal and a suitable

organism or substrate. A major criticism of these experiments is that it is difficult to extrapolate the results for enclosed laboratory organisms to those *in situ*. It is often the case that free metal ion concentration is not measured (Luoma 1983).

The toxicity of Cu to the freshwater alga, *Scenedesmus quadricauda*, was demonstrated by Petersen (1982). Using EDTA as the complexing ligand, free Cu ion was found to be toxic in the range  $10^{-10}$  to  $10^{-12}$ M. Zevenhuisen et al. (1979) found that the bacterium, *Klebsiella aerogenes*, was inhibited by concentrations of  $10^{-6}$  to  $10^{-10}$ M free Cu ion. Extracts of the bacteria were found to be highly complexing towards Cu, suggesting that organisms might modify Cu toxicity through their excretion products, exudates, murchates and soluble organic excretions. This extracellular pool, together with soil derived fulvic acids, is a possible regulator of biotic Cu toxicity (Saar and Weber 1982). Similar results were obtained by Sunda and Gillespie (1979) in a study of bacterial growth in the marine environment.

Weakly complexed Cu may also prove to be toxic. Theis and Dodge (1979) reported that  $\text{Cu}^{2+}$  and  $\text{CuOH}^+$  were taken up by the midge larva, *Chironomus tentans*, while no uptake was noted for Cu-NTA or Cu-glycine. Magnusson et al. (1979) came to the same conclusions for *Daphnia magna* and also found that carbonate complexes were not toxic. Guy and Kean (1980) showed that five organic ligands with relatively high Cu stability constants were toxic at a concentration of  $10^{-8}$ M Cu. The toxicity was higher for citric acid ( $10^{-10}$ M Cu) and ethylenediamine ( $10^{-8}$ M Cu) which have low stability constants with Cu. These small organic ligands may transport Cu into the cell tissues via the biological membrane (Luoma 1983). Copper toxicity towards fish is less at higher pH and water hardness (Borgmann 1983).

The relationship between free metal ion and toxicity is particularly relevant to soluble elements such as Zn (Spear 1981) and Cd (Ellis and Revitt 1982). Using EDTA as the complexing ligand, Allen et al. (1980) found that  $\text{Zn}^{2+}$  and  $\text{ZnOH}^+$  were the toxic species to *Microcystis aeruginosa*. Organic ligands of high molecular weight in pond water

were found to reduce Cd toxicity for *Simocephalus serrulatus*, but not for *Gambusia affinis* (Giesy et al. 1977).

Mortality for the amphipod *Hyallela azteca* correlates strongly with free Pb ion concentrations (Freedman et al. 1980). However, both the carbonate and free ionic forms of Pb have been reported as toxic to rainbow trout (Davies et al 1976).

It is thus generally accepted that the free metal ion is most toxic to aquatic life, although the exact mechanism of toxicity is not fully understood. Organic ligands seem to provide a buffer against free metal uptake. Metals bound to small organic molecules, with molecular weights less than 1000, can be assimilated by a living cell. Larger molecules represent a barrier against metal uptake, unless the metal ion is weakly complexed in which case it may be still bioavailable. Inorganic ligands may also cause a decrease of metal toxicity. This has been shown for increased hydroxyl and chloride concentrations, water hardness and alkalinity (Borgmann 1983).

The concentrations and transformations of metal species within and at the surface of organisms is of great importance (Batley 1983). It is generally accepted that metals associated with colloids are unlikely to be toxic to biota. However, Florence (1983) has stated that certain lipid soluble complexes may rapidly penetrate the membrane and cause cell death. It is unknown whether such metal complexes are present in significant concentrations in stormwater. Borgmann (1983) has noted that organic species, such as ionophores, may be readily absorbed by animal cells.

Metallothioneins are an agent for the storage and detoxification of heavy metals within the living cell. These are high molecular weight sulphur rich proteins with a high metal chelating capacity which are produced as a direct response to metal exposure. When the amount of metal ingested exceeds the synthesis of metallothionein, toxicity may occur.

Homeostatic regulation of metals can in some cases be more important than direct exposure. Zinc appears to be particularly subject to homeostatic regulation and this may explain poor correlation between metal concentrations in organisms and those in the surrounding environment (Luoma 1983).

#### 2.1.4 Water Quality Standards based on Metal Toxicity Studies.

To achieve an Environmental Quality Objective (EQO) a detailed knowledge of the behaviour of a toxic substance is required;

- a) when it enters a river
- b) concerning its effect on organisms
- c) with regard to its interaction with other organic or inorganic substances

In this way a realistic Environmental Quality Standard (EQS) can be set (Best 1982).

There are, however, major problems with this approach. It is generally assumed that metal toxicity decreases with increasing water hardness. However, Winner (1985) found that water hardness had little effect on either the acute or chronic toxicity of Cu to *Daphnia magna*. The disagreement arises from the frequent positive correlation between water hardness and alkalinity. Alkalinity may be a more important modifier of Cu toxicity (Winner 1985). Humic acid, which is not included in EQS's, causes a significant reduction of Cu toxicity to *Daphnia magna*.

Another problem is that Cu exhibits an extremely variable toxicity between species (Borgmann 1983). Even less is known about the toxicity of Zn, Cd and Pb. However, both the EEC (Mance and O'Donnell 1983) and the EPA (EPA 1983) have now set target concentrations for priority metals.

The proposed EEC values (Mance and O'Donnell 1983) quote limits for the dissolved rather than the total metal, but do not consider the effect of intermittent discharges such as stormwater inputs. Table 2.4

shows the maximum metal values for the protection of freshwater life at different hardness values (no values were given for Cd).

Table 2.4 EEC Proposed EQS Values for Protecting Freshwater Life against Heavy Metals (from Mance and O'Donnell 1983).

Total Hardness mg/l	Dissolved Pb µg/l	Dissolved Zn µg/l	Dissolved Cu µg/l
0-50	50	70	1
50-100	125	170	6
100-150	125	250	10
150-200	250	250	10
200-250	250	250	10
250+	250	500	28

The EPA (EPA 1983) criteria, however, take into account the effect of intermittent total metal discharges (Table 2.5). Although somewhat higher than continuous discharge levels, they provide a more realistic basis for the assessment of stormwater impacts. Receiving water dilution of stormwater runoff can substantially decrease metal concentrations, although small urban streams carry only slightly diluted storm runoff (Cole et al. 1984).

Exceedance of the significant mortality levels has been noted by Cole et al. (1984) for Cu in 50% of their U.S. nationwide samples and also for Pb (27%). Threshold values are exceeded for all metals to some extent; Pb (96%), Cu (87%), Zn (78%) and Cd (55%). These exceedance frequencies can be compared to values calculated from the data base of Malmqvist (1983) in the Bergsjön catchment. For individual storm events Cu always exceeded threshold values, while Zn (53%) and Pb (63%) exceeded less often than in the U.S. nationwide survey. The

acute levels were exceeded by all three metals; Zn (11%), Pb (16%) and particularly Cu (95%).

Table 2.5 EPA Water Target Concentrations,  $\mu\text{g/l}$  Total Metal (from EPA 1983).

Heavy Metal	Total Hardness mg/l	Freshwater Toxic Criteria $\mu\text{g/l}$		Intermittent Discharge Criteria $\mu\text{g/l}$	
		24 Hour	Maximum	Threshold	Significant Mortality
Copper	50	5.6	12	20	50-90
	100	5.6	22	35	90-150
	300	5.6	62	115	265-500
Zinc	50	47	180	380	870-3200
	100	47	321	680	1550-4500
	300	47	800	1700	3850-11000
Cadmium	50	0.01	1.5	3	7-160
	100	0.02	3.0	6.6	15-350
	300	0.08	9.6	20	45-1070
Lead	50	0.75	74	150	350-3200
	100	3.8	172	360	820-7500
	300	50.0	660	1400	3100-29000

LaPoint et al. (1984) found that in some cases polluted streams had a change in the benthic fauna due to nutrient and organic excesses rather than metal impaction. The metal concentrations in some streams in the U.S. greatly exceed EPA standards and yet have a relatively

healthy, if restricted, biota. Urban streams often have a turbulent, highly oxygenated flow which might help to support a diverse metal tolerant population (Ellis 1985). It was suggested by LaPoint et al. (1984) that the EPA criteria may be over-stringent as they are based on toxicity evidence from only a few sensitive aquatic species. However, their own results generally showed that control zones had a statistically higher species richness and invertebrate abundance than metal polluted zones.

#### 2.1.5 Heavy Metal Speciation in Urban Runoff: Sources and Toxicity.

Whilst the contributing sources of heavy metals within the urban catchment are still somewhat speculative, it is now widely accepted that the levels of these priority pollutants in storm runoff can be substantial. Metals are likely to undergo physical and chemical speciation changes during their transport over the urban surface and through the below ground system. The chemical processes which could act on metal speciation include; pH changes, variations in reducing or oxidising conditions, organic and inorganic ligand concentrations, ionic strength.

It is not known whether the resulting metal species exert a toxic effect on receiving stream habitats. However, increasing urbanisation seems to lead to increased metal levels in the fauna of streams receiving stormwater runoff (Ellis et al 1985). Progress in the study of speciation in natural water systems is now sufficient to enable a differentiation of potentially toxic heavy metal species in urban stormwater. Large fluxes of toxic heavy metal species from stormwater discharges may well be hazardous to both the fauna and the flora of a receiving stream. The determination of metal impact can be aided by the use of water quality standards together with an appreciation of the toxicity of the metal species present.

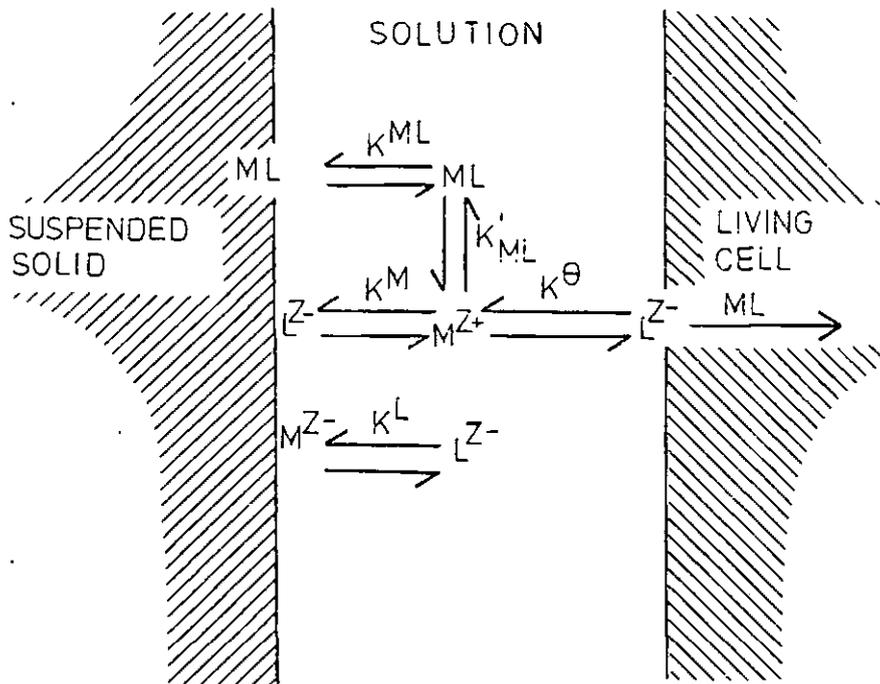
## 2.2 Theoretical Aspects of the Speciation of Heavy Metals in Natural Waters.

Heavy metals in aqueous systems may occur as organic and inorganic complexes of varying sizes, or be associated with particulate materials of a heterogeneous nature. Stumm and Brauner (1975) and Steinnes (1983) have outlined the various forms in which metals are thought to exist in seawater (Table 2.6). An important problem, which relates to most natural aquatic systems, is the difficulty of distinguishing between dissolved and particulate species using conventional physical methods, such as filtration.

Theoretical considerations of metal speciation have been developed by Buffle (1981). Dissolved ligands, living cells and suspended solids compete for metals under certain thermodynamic and kinetic constraints. The complexity of this system is partly illustrated in Figure 2.1. Metal ligand complexes have a metastable relationship with the free metal ion as well as living cells and suspended sediment particles. Despite the progress which is being made with the measurement of the different stability constants there is still a lack of certainty concerning their values. The approach suggested by Buffle (1981) using these constants indicates that the free metal ion only competes for the living cell, whilst both the free metal ion and metal complex can attach to the suspended solid. The ligands that interact with the metal ion can be either organic or inorganic.

Table 2.6 The Size Spectrum and Associations of Metal Species in Natural Waters (from Stumm and Brauner 1975, Steinnes 1983).

Phase	Species Present	Diameter Range (Molecular Weight)
Dissolved	Inorganically complexed metals. Metals complexed with small organic molecules. Free metal ions.	0-0.8 nm (0-150)
Colloidal	Metals associated with organic/ Fe oxide colloids. Metals complexed with organic fibrils.	0.8-400 nm (150-10 <sup>7</sup> )
Suspended Solids and Particulates	Carbonate bound metals. Metals adsorbed onto or bound to Fe and Mn hydrous oxides. Organically complexed metal species. Metals adsorbed onto, or contained within the lattice of, clays, sands and silts.	> 400 nm (> 10 <sup>7</sup> )



M=Metal, L=Ligand, K=Dissociation Constant,  $K^{ML}$ =Adsorption of ML on Solid,  $K^L$ =Adsorption of L on solid,  $K^M$ =Adsorption of M on solid,  $K^\theta$ =Adsorption of M on cell membrane,  $K'^{ML}$ =Stability constant of M and L in solution,

Figure 2.1 The Most Relevant Reactions of a Toxic Metal in a Water Sample (after Buffle 1981). Diffusion Rates are not included.

These theoretical considerations are a useful basis for the determination of toxic or bioavailable metal species. An exact separation of all the chemical species would be beyond the reach of present speciation techniques, but a determination of toxic metal could be of considerable value for the screening of wastewaters and

storm effluents and in developing in-stream standards for water quality objectives.

### 2.3 Instrumentation for Speciation Studies.

The development of sensitive analytical techniques suitable for the measurement of heavy metals at trace levels ( $10^{-6}$  to  $10^{-10}$ M) has been of obvious importance in the determination of heavy metal species. Some techniques are particularly suitable for speciation studies. A differentiation of chemical species, such as free metal ions, from total metal can be achieved by Ion Selective Electrodes or Anodic Stripping Voltammetry (ASV). A preliminary separation technique, followed by instrumental analysis is also satisfactory and Graphite Furnace Atomic Absorption can be used as a sensitive detector.

#### 2.3.1 Ion Selective Electrodes.

The species-specific nature of metal Ion Selective Electrodes which respond only to the activity of the free (hydrated) metal ion, has attracted widespread interest (Florence and Batley 1980). The limiting factor in these techniques is the non-linear response of the electrode to metal activity below  $\approx 10^{-6}$ M, although measurements in the non-linear region can be made with proper calibration (Midgley 1981) and concentrations as low as  $10^{-10}$ M have been monitored in the presence of metal buffers (Avdeef et al. 1983).

The most commonly used electrode for trace metal detection is the Cu electrode. Cadmium and Pb Ion Selective Electrodes have been found to be unsuitable for natural water analysis (Florence and Batley 1977). However, with the attainment of lower detection limits due to an understanding of interferences and electrode response to pH and ionic strength changes, a more widespread use of Cu, Cd and Pb electrodes is possible.

Some early studies have applied the technique to Cu in seawater (Blaedel and Dinwiddie 1974, Jasinski et al. 1974). The technique has

been found to be unreliable for coastal water samples due probably to interference by chelating agents (Jasinski et al. 1974) and the same problems might be expected in polluted waters with a high organic content.

The detection limit for the Cu electrode is sufficiently low to allow the analysis of the metal in many polluted waters. The limit of detection is determined by the solubility of the electrode materials (Midgley 1981) and in particular the membrane (Jain and Schultz 1984). It is important to satisfy the experimental conditions so that only a Cu ion response is obtained, as this can be affected by the physical state of the electrode surface and the chemical environment within which the electrode is working (Frazer et al. 1983). Changes in pH and ionic strength can have a dramatic effect on the electrode response and it is therefore necessary to take these into account when using Ion Selective Electrodes to monitor environmental samples.

### 2.3.2 Anodic Stripping Voltammetry.

ASV in the differential pulse mode is sufficiently sensitive, with a typical detection limit of about  $10^{-9}M$ , for the direct determination of heavy metals in natural waters (Florence 1982a). This analytical technique has an intrinsic capability for speciation work due to the distinction of the electrochemically available fraction, which may be toxic, and the bound or electrochemically inert fraction which is less likely to demonstrate toxic properties.

#### 2.3.2.1 Theoretical Considerations.

ASV initially involves a bulk electrolysis step (pre-electrolysis) to concentrate the desired metals into the small volume of a Hg electrode. The Hg electrode may be either a hanging drop or thin film type. Following this electrodeposition step, the material is redissolved or stripped from the electrode using differential pulse or linear sweep voltammetry and the current recorded. If the conditions during pre-electrolysis are constant then exhaustive electrolysis of

the solution is not necessary and, by proper calibration utilising fixed electrolysis times, the measured voltammetric response can be employed to find the solution concentration.

The redox procedure allows the differentiation of metal species at low levels and during the plating step the potential can be set so that certain metal species are not reduced. In the stripping process the peak potential will depend on the metal species present and hence the following equations (equations 2.1-2.3) apply;

#### Deposition (plating) step



#### Stripping step



ML= Species of interest,  $M^{2+}$ = Aquo metal ion,  $L^{2-}$ = Free ligand,  $k_r$  and  $k_b$  = Rate Constants.

The contribution of a metal complex species (ML) to the ASV peak height or current relative to that of the free metal ion, depends on the rate constant for the dissociation of the complex and the thickness of the diffusion layer. Diffusion layer thickness depends on the stirring rate and therefore the thicker the diffusion layer, the higher the contribution of a metal complex to the ASV wave height (Florence 1982a). No research work has been reported concerning the determination of diffusion layer thickness ( $\delta$ ) which requires a well defined rotating disc electrode to enable  $\delta$  to be calculated as a function of the rotation speed (Whitfield and Turner 1979).

### 2.3.2.2 Application of the Technique and its Problems.

ASV has commonly been applied to the primary distinction between "labile" and "bound" metals in filtered water samples (Chau and Lum-Shue-Chan 1974, Duinker and Kramer 1977). The normal procedure for estimating the fraction of labile or electrochemically available metal involves a standard addition analysis of an untreated sample and is therefore dependent on the kinetics of the reactions controlling the assimilation of the metal spike (Whitfield and Turner 1979). Labile metal, as defined by the experimental conditions, therefore includes ionic as well as some weakly complexed metal. Bound metal is identifiable as the non-labile fraction and is typically associated with a variety of organic and inorganic colloidal materials (Batley and Florence 1976a).

Astruc et al. (1981) have stated that there is a need to replace the "lability" concept with equilibrium and rate constant values. Whitfield and Turner (1979) have suggested that this is possible with a rotating disc electrode, although most measurements have been made with hanging Hg drop electrodes.

There are a number of problems pertaining to the ASV analytical procedure which must be considered;

a) Surface active compounds (surfactants) may adsorb on the Hg electrode causing metal peak interference (Florence 1982a).

Surfactants, although not altering the peak position, have been found to enhance Cu and Pb peaks by 20% and 10%, respectively and to suppress Cd responses at concentrations in the mg/l range (Beveridge and Pickering 1984). At the  $\mu\text{g/l}$  level of even relatively polluted waters, the low concentrations of surfactants would not be expected to have a significant effect on observed ASV peaks, especially considering sampling variability in conjunction with the ASV precision. Metals can therefore still be determined in the presence of surfactants, provided the standard addition approach is used.

b) Tensammetric waves arise as a result of adsorption-desorption processes at the Hg electrode and have been mistaken for Cd, Pb or Cu

peaks in seawater analysis. Natural organic compounds in seawater give rise to these tensammetric waves which, at pH 5.0, occur near the Pb and Cd peaks. However, they do not appear if a simple linear voltage scan is used (Florence 1982a).

c) In practice, the removal of oxygen by bubbling nitrogen through the sample is necessary to prevent interference on the polarogram. In poorly buffered waters this may cause a large pH increase, due to carbon dioxide evolution, and a resulting change in metal speciation. This problem can be overcome by the addition of a suitable buffer or by flushing with a suitable  $N_2/CO_2$  gas mixture. Sodium acetate is probably the most commonly employed buffer but cannot be considered to be completely non-complexing.

d) As ASV is an electrochemical procedure a base electrolyte must be employed if the sample does not already have an ionic strength of at least 0.02M. Many natural waters do not meet this requirement and, therefore, the addition of  $KNO_3$  or KCl may be considered.

e) Copper forms an intermetallic compound with Zn resulting in an overestimation of the Cu concentration. To overcome this problem Zn and Cu must be determined separately.

#### 2.3.2.3 Comparison of ASV Measurements with a Model Cell.

Whitfield and Turner (1979) have reported two concepts that have been used to provide chemical analogues of the biological availability of trace metals.

a) Thermodynamic availability; this relates to the activity of the particular form that is taken up preferentially by an organism.

b) Electrochemical availability; this is the fraction of the total metal concentration that is available for electro-deposition at an electrode immersed in the solution during the timescale of the plating process.

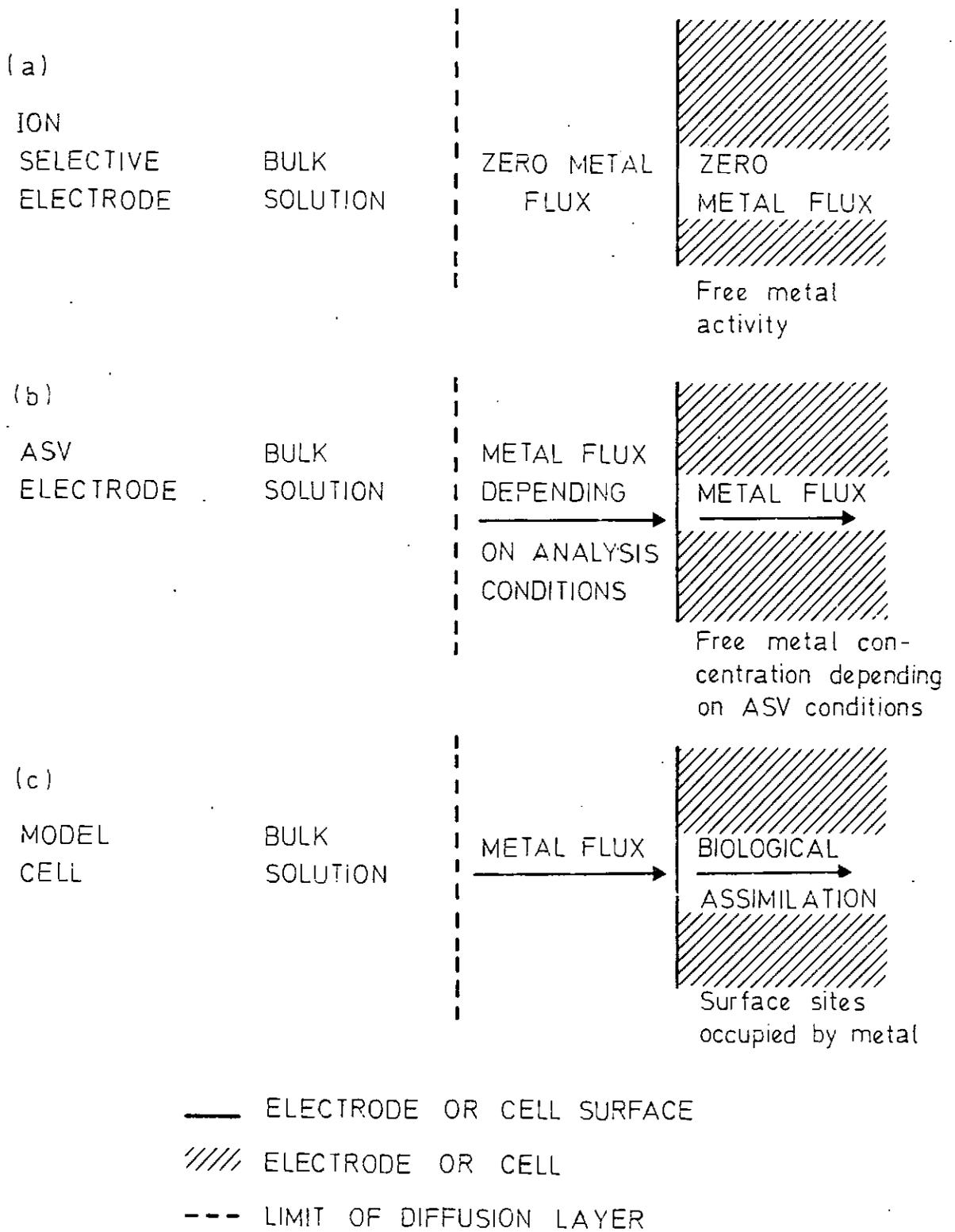


Figure 2.2 A Comparison of the Conditions during the Sensing of Metal Ions at Two Electrode Systems and a Model Cell (from Whitfield and Turner 1979).

Figure 2.2 illustrates (a) the reactions occurring at an Ion Selective Electrode, (b) at the ASV hanging Hg drop or Hg film and (c) at the surface of a model biological cell. The membrane of the Ion Selective Electrode simply senses the free metal ion without accumulation and hence the metal flux ( $J$ ) is zero. The accumulation of metal ion at the model cell is not comparable to this system. On the other hand, ASV shows a metal flux ( $J_k$ ) which depends on the conditions employed in the analysis. If the diffusion layer thickness ( $\delta$ ) is known then a useful comparison with the metal flux at the model cell can be made. However, it is important to realise that the transport of metal into the cell is dependent on membrane conditions whilst, in ASV the limiting condition is the metal flux in the diffusion layer and consequently uptake by the model cell is comparatively low.

Although some features of the model cell cannot be reproduced electrochemically, e.g. surface adsorption sites, the work of Whitfield and Turner (1979) suggests that electrochemically available metal may relate to bioavailable metal. However, it should be remembered that ASV does measure some species which are unavailable to biota e.g.  $\text{CuCO}_3$  (Luoma 1983). Despite this the model does provide a useful analogy between the bioavailable and electrochemically available metal forms.

### 2.3.3 Graphite Furnace Atomic Absorption.

Although the technique is non-species selective, Graphite Furnace Atomic Absorption is an automated sensitive technique suitable for measuring total metal concentrations (Astruc et al. 1981). It can be used, in conjunction with a preliminary separation process, to provide information on metal speciation. Gas Chromatography for volatile organo-metallics (Fernandez 1977, Van Loon 1979) and separation on the basis of size or charge (Guy and Chakrabarti 1976) are typical first steps.

Inductively Coupled Plasma techniques are now being increasingly used, with the high temperature plasma as a spectral emission source. With

comparable detection limits to Graphite Furnace Atomic Absorption the main advantage is application in simultaneous multi-element analysis (Pinta 1978).

#### 2.3.4 Other Analytical Techniques.

Neutron Activation Analysis and X-ray Fluorescence can be used to detect heavy metals, although their applications to speciation are limited.

##### 2.3.4.1 Neutron Activation Analysis.

The radioactive properties of a nuclide can be utilised to detect an element using Neutron Activation Analysis. After bombarding a sample with neutrons in a reactor the induced activity is compared with standards to provide both qualitative and quantitative results. The technique is very sensitive providing that all the samples and standards are irradiated in the same particle flux. With water samples it is usually necessary to carry out a preliminary separation step to remove Na, Mg and P, which interfere and decrease the precision of the technique. Total metal concentrations are measured by Neutron Activation Analysis, although de Jong and Wiles (1976) have used the method to determine methylmercury in fish.

##### 2.3.4.2 X-ray Fluorescence.

Total heavy metals can also be determined by X-ray Fluorescence. This is a highly sensitive technique which has recently been incorporated into a speciation scheme for heavy metals in river water (Pik et al. 1982). Particulate material is analysed directly by thin film X-ray Fluorescence, while determination of the dissolved phase requires co-precipitation of the metals before analysis. The low detection limits of this method (Cd = 0.1 µg/l, Pb = 1.6 µg/l) suggest the possibility of a more widespread use of X-ray Fluorescence in future speciation schemes.

### 2.3.5 Assessment of the Instrumentation Techniques Applicable to Speciation Work.

A direct measurement of bioavailable heavy metals is highly desirable for the rapid screening of wastewaters. Whitfield and Turner (1979) demonstrated that direct ASV analysis is more representative of the bioavailable fraction than Ion Selective Electrodes, although the comparison of an electrochemical cell with a model biological cell can only be a theoretical one. Atomic Absorption, Neutron Activation Analysis and X-ray Fluorescence measure only the total heavy metal and therefore the sample requires suitable preliminary separation techniques before metal analysis.

### 2.4 Procedures for the Physical and Chemical Separation of Heavy Metals in the Dissolved Phase.

The preliminary separation of heavy metals according to physico-chemical characteristics has been carried out in a variety of ways. Ion exchange resins which are selective for heavy metals may be used to remove the toxic metal species, whilst organically bound metals can be released by several different oxidation procedures. Separation on the basis of size allows the differentiation of dissolved, colloidal and particulate associated metal species. The different approaches are complementary to each other providing a wide range of information on metal speciation.

#### 2.4.1 Ion Exchange Techniques.

The introduction of heavy metal selective ion exchange resins has provided an important step forward in speciation studies. It is thought that these resins may provide some indication of bioavailable metal and if such a resin can be developed then it could find a valuable use in the removal of toxic metal species from wastewaters.

Chelex-100 is known to take up the free metal ion and weakly complexed metals. Thiol resins may more closely resemble the natural uptake of

metal ions; certainly more Cu is removed by this resin (Florence 1982b). Cellulose chelating exchangers provide a quantitative removal of metals from the aqueous environment, although species-specific chelating groups might usefully be attached to the cellulose.

Ion exchange separations have been used in speciation schemes to separate cationic from anionic metal species (Ramamoorthy and Morgan 1983), although Batley (1983) has stated that such separations probably have little biological relevance.

#### 2.4.1.1 Ion Exchange Theory.

The uptake and storage of metal ions by sorbent ion exchange resins is shown in Figure 2.3. The metal ion may adsorb either to the resin surface or, after diffusion, to the pore surface. A strong diffusion gradient allows the transport of metal ions into the resin pores due to the rapid chelation of metal by the resin. The resin structure is homogeneous down to 0.5-1.0 nm and so should prevent the entry of colloids.

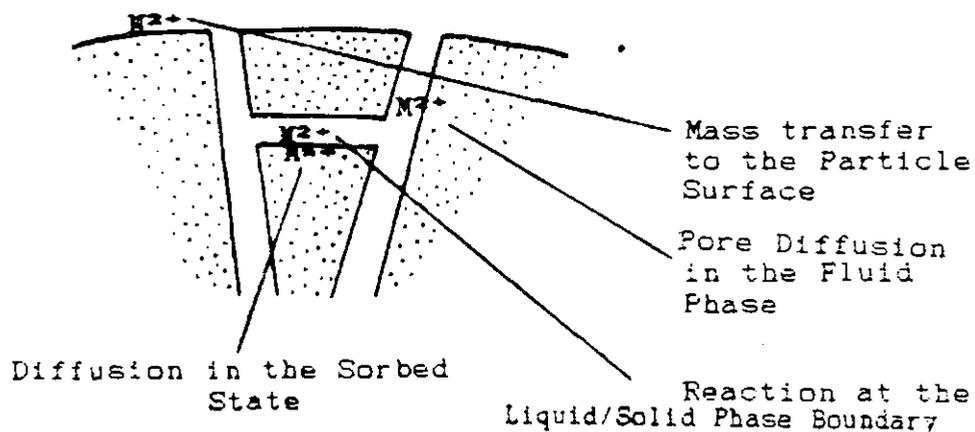


Figure 2.3 Uptake and Diffusion of Metal Ions onto and around an Ion Exchange Resin (from Perry and Chilton, 1982).

Equilibrium behaviour of metal ions with an ion exchange resin can be described by plotting metal concentration in the solid phase against

metal concentration in the liquid phase (Figure 2.4). The experiment is carried out by the titration of a constant metal concentration onto the resin, contained in a column, and measurement of the eluant metal concentration.

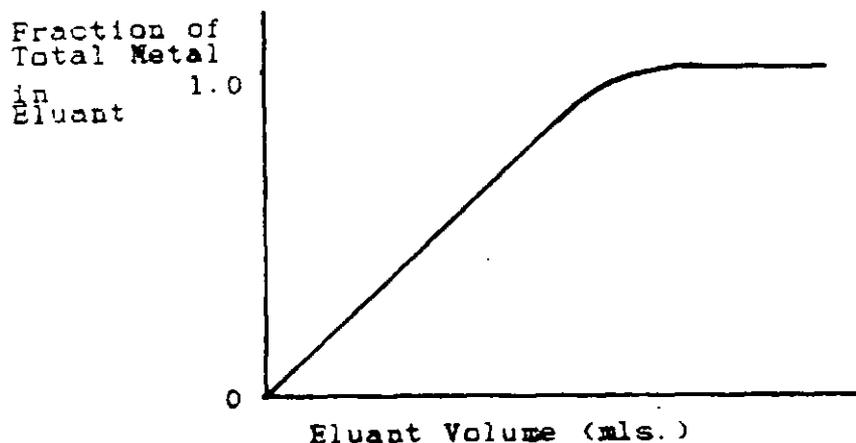


Figure 2.4 Langmuir Isotherm describing Metal Uptake Equilibrium with an Ion Exchange Resin.

The Langmuir Isotherm, shown in Figure 2.4, applies to ion exchange on completely homogeneous surfaces. The curve is linear near the origin and shows a constant separation until saturation is reached.

#### 2.4.1.2 Chelex-100 Chelating Resin.

This resin has been successfully applied to seawater metal analysis (Riley and Taylor 1968, Florence and Batley 1976). The resin contains an iminodiacetate chelating group which is highly sensitive for heavy metals. These are strongly complexed by the oxygen and nitrogen atoms of the iminodiacetate groups, but it is mainly only the ionic form of the metal which is taken up due to the small pore diameter of the resin (1.5 to 3 nm). The stability of the iminodiacetate groups ( $\log K = 13$  for Cu) is such that weakly complexed metals may dissociate and preferentially associate with the Chelex-100. The ionic

form retained by the resin represents the more readily bioavailable metal, whilst the organically coated colloidal particles which are excluded are nevertheless considered to be potentially available for metal solubilisation and transport.

An alternative theory concerning the uptake mechanism of metals by Chelex-100 has been put forward by Figura and McDuffie (1979). The slow dissociation of metal complexes in solution, rather than molecular exclusion, is stated to be the cause of the incomplete retention by Chelex-100 of some trace metals in natural waters. Hence the non-uptake of highly stable metal-NTA complexes by Chelex-100 complexes may be due to slow resin kinetics. The time scale of metal lability for Chelex-100 may be a few seconds, compared to ASV where the contact time, of a small proportion of the sample solution, with the electrode surface is only a few milliseconds (Cox et al. 1984).

Two experimental approaches for the use of Chelex resin have been tested:

- a) Resin bed in a column; metal ions are taken up as the water sample passes down the column at a known flow rate, typically 1-2 ml/min (Florence and Batley 1975, Montgomery and Santiago 1978). Blocking of the columns due to the swelling characteristics of Chelex-100 is a common problem with this technique.
- b) Batch technique; longer contact times, up to 16-24 hours, are employed enabling full equilibration of resin and sample metals to be reached (Hart and Davies 1977). The method has proved useful in identifying colloidal associated metals on the basis that these are not kinetically labile during the batch experiment (Figura and McDuffie 1980). A criticism of the method is that displacement of chemical equilibria may occur so that chelates that are sufficiently labile may be displaced (Astruc et al. 1981).

In order to maintain stable pH conditions in the sample and to carry out the experiment over a wide range of pH values the Ca form of Chelex-100 is now preferred (Figura and McDuffie 1977) compared to the Na (Hart and Davies 1977) and H (Florence and Batley 1975) forms.

The efficiency of Pb recovery from tap water by Chelex-100 has been studied by de Mora and Harrison (1983b). Even in the batch mode, Chelex-100 could not remove all the metal present, although a poly(maleic anhydride) resin did exhibit a 100% removal efficiency. This can be explained by the greater affinity of the poly(maleic anhydride) resin for strongly complexed Pb species.

Despite problems with the interpretation of the results in terms of the levels of toxic metal, the use of Chelex-100 is a flexible technique which allows the concentration of a variety of metal ions over a wide pH range to be determined. A simple separation by either the Column or Batch technique is rapid, inexpensive and with care presents little opportunity for contamination.

#### 2.4.1.3 Thiol Chelating Resins.

Recently Thiol based materials have been used successfully to remove Zn, Cd, Pb and Cu from natural waters (Florence 1982b). The presence of chelating sulphhydryl groups has been shown to correlate with heavy metal toxicity (Fisher and Price 1981) and on this basis the metal fraction removed by the thiol group is considered to be a realistic estimate of bioavailable metal (Florence 1982b). The transportation of metals across a cell membrane is believed to be dependent on the lipid solubility of metal species. Similarities between metallothioneins and membrane carrier proteins (Cherian and Goyer 1978, Koyima and Kagi 1978, Lerch 1980, Roesijaldi 1980) suggest that metals may be complexed and transported in association with sulphhydryl groups. This process may be simulated using a Thiol resin and it has been reported that thiol materials generally have a lower affinity for Pb, Cd and Zn, but a higher affinity for Cu, than Chelex-100. The order of selectivity at pH 5.5 is Cu(II) > Pb(II) > Cd(II) > Zn(II).

Florence (1982b) has reported metal speciation results for a thioglycollate chelating resin which was initially prepared by Phillips and Fritz (1978). The resin contains the thioglycoloxymethyl chelating group (-CH<sub>2</sub>OCO-CH<sub>2</sub>SH) attached to the benzene ring of a

polystyrene-divinylbenzene resin (XAD-4). The use of 500 mg resin/ 50 ml of sample is considered to be suitable for a batch extraction. The sulphur content of the prepared resin is generally 1.87 mmol/g and heavy metals form a 1:2 complex with the mercapto group of the resin (Phillips and Fritz 1978).

#### 2.4.1.4 Chelating Cellulose Exchangers.

Cellulose exchangers have been used to remove heavy metals from water samples by attaching suitable chelating groups. Hyphan is a cellulose chelating exchanger which is selective for heavy metals at trace levels. Using this material Burba and Willmer (1982a, 1982b) found that heavy metals were recovered from seawater to the extent of 80-100%. In simulated aqueous samples the metals were stripped off humic acids, but were not removed from EDTA complexes. Such a distinction could be useful in speciation studies, although Chelex-100 has been more widely chosen.

#### 2.4.1.5 Comparison of Metal taken up by Chelating Resins with Toxicity to Biota.

It is possible to attach organic groups to ion exchange resins which closely imitate those metal chelators found in a biological cell (Florence 1982b). Florence et al. (1983) have compared the growth rate of an alga, *Nitzschia closterium*, in seawater, with the concentration of the Cu fractions removed by various chelating resins.

Chelex-100 and Thiol resins using the column method, as well as direct ASV analysis at -1.3V, were found to overestimate the toxic Cu fraction. ASV-labile measurements at -0.6V compared more favourably to the toxic fraction when colloidal type ligands were added. Electrochemical deposition of Cu at -1.3V can therefore liberate non-bioavailable Cu from certain complexes which is not released at -0.6V.

## 2.4.2 Techniques for the Measurement of Organically Associated Metals.

Several methods, both chemical and physical, have been used to decompose organic materials in natural waters. Some organic compounds are highly resistant and require extensive oxidation before their heavy metals are released.

### 2.4.2.1 Ultra-Violet Irradiation.

The decomposition of organic compounds in natural waters by ultra-violet irradiation was introduced by Armstrong et al. (1966) for the determination of organic carbon in seawater and was subsequently used by other workers to release organically associated heavy metals (Florence and Batley 1977, Laxen and Harrison 1981a). The sample, usually 150 to 200 ml, is introduced into quartz tubes and, after the addition of a few drops of 30%  $H_2O_2$ , is irradiated for four to eight hours with a medium pressure ultra-violet lamp of between 500 and 1000W.

The method has had most success in seawater analysis because, in freshwaters, Fe hydroxide is released from an organic colloidal coating and co-precipitates the heavy metals (Laxen and Harrison 1981b, Florence 1982a). It should be possible to dissolve the precipitate in 1M  $HNO_3$  prior to analysis although this has not been tested. Heavy metals will rapidly adsorb onto the surface of the quartz tubes during cooling and therefore immediate analysis is recommended.

### 2.4.2.2 Adsorption of Organics by Resins.

SM2 and XAD-2 are divinylbenzene resins with a high surface area which can adsorb organic material from aquatic samples. It is possible to remove lipid soluble metal from a variety of water samples using SM2 or XAD-2 (Florence 1982b). The analysis is carried out at pH 4.0 to

prevent free metal ion adsorption to the resin. Following adsorption, the lipid associated metals are either eluted with methanol and decomposed by wet acid oxidation (Florence 1982b) or the resin and organics are decomposed by a dry ashing procedure (Montgomery and Santiago 1978). These resins may be useful for the assessment of lipid soluble metal species (Florence 1983).

#### 2.4.2.3 Solvent Extraction.

Solvent extraction separates metal species on the basis of their polarity (Batley 1983) and can therefore represent those species that are lipid soluble (Florence 1983). A 9:1 hexane-butanol mixture has a similar dielectric constant to the cell membrane lipid bilayer (Batley 1983).

#### 2.4.2.4 Oxidation by Concentrated Acids.

Organic material can be completely oxidised by the addition of suitable concentrated acids. Chau et al. (1974) used a persulphate/sulphuric acid oxidising mixture, while Florence (1977) used a mixture of perchloric and nitric acids. In seawater, a reduction to pH 2.0 followed by boiling for 15 minutes is usually sufficient to liberate all the heavy metals (Florence and Batley 1977).

Bourcier and Sharma (1980) found no significant difference for heavy metal concentrations after the digestion of stormwater solids with either HF/HNO<sub>3</sub> or HCl/HNO<sub>3</sub> mixtures. In the Middlesex Polytechnic Urban Pollution Research Centre a mixture of concentrated perchloric and nitric acids in a ratio of 1:9 is used as a standard method for the organic degradation of both sediments and filtered water samples (Revitt et al. 1981).

#### 2.4.2.5 Decomposition of Organics by Ozonolysis.

The use of ozone to decompose organics in natural waters has been investigated (Laxen and Harrison 1981a) and shown to give an

unexpected decrease in the levels of electrochemically available metals. In the case of Pb it was suggested that this was due to the precipitation of the metal as  $PbO_2$  after ozone oxidation of Pb(II) to Pb(IV).

#### 2.4.3 Differentiation of Metal Species by Size Separation.

Heavy metals may be associated with dissolved, colloidal or particulate phases. The accepted separation of the dissolved phase by 0.4  $\mu m$  or 0.45  $\mu m$  filtration often results in clogging of the filters due to the presence of organic and inorganic colloids (Astruc et al. 1981). Another approach for separating metal fractions is therefore to discriminate on the basis of molecular size or molecular weight by either centrifugation, filtration, ultrafiltration or dialysis. Size fractionation can be used to complement other physico-chemical separation methods (de Mora and Harrison (1983a).

##### 2.4.3.1 Centrifugation.

The speed and time of centrifugation determines the quantity of particulates removed from suspension, the separation depending not only on size but also on density. This makes an efficient comparison with other physical separation techniques difficult. Centrifugation at 3000 rpm for 30 minutes has been shown to separate particles smaller than 190 nm (Benes and Steinnes 1975) whilst centrifugation at 40000 rpm for up to five hours may remove humic substances (Buffle et al. 1978, Steinnes 1983).

##### 2.4.3.2 Dialysis.

Dialysis allows the separation of different groups of species on the basis of particle size (Buffle 1981). Typically ultra-pure water in a dialysis bag is allowed to equilibrate with the sample for 24 hours (Guy and Chakrabarti 1976). Under these conditions and with a pore size of one to five nm (molecular weight cut-off value  $\approx$  1000) it is found that free dissolved metal ion concentrations inside and outside

the dialysis bag are equal. An alternative approach is to place the bag *in situ* for 1 to 14 days until the adsorption equilibrium is reached. Dialysis *in situ* does not suffer from the problems of normal dialysis, i.e. adsorption to the membrane walls, as equilibrium with the surrounding water is reached. A receiving chelator, such as an ion exchange resin, can reduce the length of the equilibration time from a few days to a few hours (Steinnes 1983).

Hart and Davies (1981) have incorporated a semi-continuous process into their speciation scheme in which a dialysis unit was coupled with a Chelex-100 column. This system was found to reduce the time of equilibration to five hours.

Cox et al. (1984) have compared the effect of different receiving electrolytes contained within a cation exchange membrane. The cation exchange membrane prevents the flux of slowly diffusing anions, giving an equilibration time of less than one hour. Receiving electrolytes included 0.3M HCl, which liberates metals from weak complexes at the membrane/analyte interface, and 0.05M EDTA which chelates metals and creates a metal diffusion gradient across the membrane.

It was argued that the dialysis process may realistically represent bioavailable metal uptake, as it is also a membrane transfer process. Cox et al. (1984) found that dialysis gave similar results to a sulphonate ion exchanger, but gave lower results when compared to uptake by Chelex-100 resin.

Dialysis could be combined with a receiving chelating resin to imitate the metal uptake process in a biological cell. the receiving resin should be chosen to provide the same functional chelating groups found in cell constituents.

Electrodialysis involves acceleration of metal passage through the dialysis membrane by applying a potential gradient (Steinnes 1983). This method has not been widely used to speciate metals in aquatic samples, but could provide a rapid electrochemical size separation.

#### 2.4.3.3 Filtration.

A single filtration step, through a 0.4  $\mu\text{m}$  or 0.45  $\mu\text{m}$  filter is often employed as a preliminary separation for the dissolved and particulate phases. However, this separation is complicated by the presence of colloids (Stumm and Brauner 1975). Laxen and Harrison (1981a) have introduced a speciation scheme using a series of five nucleopore filters ranging in pore size from 12  $\mu\text{m}$  to 0.015  $\mu\text{m}$ . Nucleopore filters act as barrier, rather than depth, filters allowing a very effective cut-off value and few adsorption losses (Sheldon 1972). In a recent review of size separation techniques de Mora and Harrison (1983a) recommended the use of filtration as a useful comparison to other speciation techniques.

#### 2.4.3.4 Ultrafiltration.

Benes and Steinnes (1974) pioneered the use of ultrafiltration in speciation work. Ultrafiltration can be defined as the separation of metal fractions by filtration below 0.015  $\mu\text{m}$ .

Ultrafiltration cannot be exactly related to molecular weight as the ultrafiltered fractions are separated not only on the basis of size, but also shape and charge characteristics (Guy and Chakrabarti 1976). Nevertheless the sizes for metal species can be compared with typical cut-off values for ultra-filters. The Amicon PM10 filter has a pore size of 1.8 nm and should permit the separation of free metal ions and small organic and inorganic complexes resulting from trace metals associated with humic substances and colloidal species. Laxen and Harrison (1981a) incorporated this single ultrafiltration step in their filtration based scheme.

A cascade system of ultrafilters, or sequential ultrafiltration, can be used to reduce the adsorption of high molecular weight compounds by preventing their contact with small pore size materials. Hoffmann et al. (1981) found that large concentration gradients could be avoided by only filtering the first 50% of the sample at each step and hence

avoiding the need for repeated washings. To calculate the concentration of metals in each molecular weight range a system of mass balance equations was formulated.

The main problems relating to ultrafiltration are as follows:

- a) the membranes are expensive.
- b) the filters as supplied are often contaminated with metal and soluble organic material.
- c) contamination and adsorption losses in ultrafiltration are especially serious because there is a large surface to volume ratio.
- d) the concentration gradient at the surface of the membrane filter may cause dissociation of colloiddally associated metals and changes in ionic strength.
- e) The trapping of particles in the pores of filters make the separations difficult to achieve and consequently result in long filtration times.

Despite recent advances in ultrafiltration this technique is still open to criticism. Nominal molecular weight cut-offs are imprecise making the interpretation and comparison of results difficult. The technique is expensive requiring a new membrane for each filtration and the long filtration times inhibit the handling of large numbers of samples. Because of these problems de Mora and Harrison (1983a) prefer dialysis to ultrafiltration on the basis of cost, speed of analysis and efficiency of separation.

#### 2.4.4 Other Separation and Analytical Techniques

Several alternative methods of separation and analysis have been tested and, although not often used, these techniques can be useful for comparison with the more generally accepted methods. For example metal ion catalysis is very specific to the free ion and should compare with other free ion measurements such as Anodic Stripping Voltammetry or dialysis.

#### 2.4.4.1 Metal Ion Catalysis.

During the metal ion catalysis of oxidation-reduction reactions the rate of the reaction is directly proportional to the free metal ion concentration. An example of such a system which has been studied is the catalytic effect of Cu on the oxidation of L-ascorbic acid (Mottola et al. 1968). Ferrer-Herranz and Perez-Bendito (1981) devised a method, based on this technique, for the determination of Cu in water at the 10-90 µg/l level and Nakano et al. (1981) used a similar approach for Cu in tap water. A method which is free from interferences has been devised for the determination of Zn in water samples (Haraguchi et al. 1980). The presence of Zn causes a difference in the rate of the ligand substitution reaction between 1-(2-thiazolylazo)-5-naphthol chelates and EDTA.

However, the method has been avoided in natural waters, despite its specificity for free metal ion, as it is thought that catalysts or inhibitors in the sample may affect the accuracy of the determination.

#### 2.4.4.2 Radiotracers.

Radiotracers can be added to a sample as a means of tracing the species which a heavy metal can form. Attempts to use ionic radiotracers have been hindered by the slow equilibration of the labelled ions with the non-ionic species of the heavy metal in the sample (Benes and Steinnes 1976). The equilibration period may be of the order of months or even years (Bowen et al. 1979).

#### 2.4.4.3 Gel Filtration Chromatography.

For polluted waters Gel Filtration Chromatography may be an alternative method for separating metals into molecular size fractions (Steinberg 1980). Sample or solute flow is retarded in relation to eluant on a column of porous polymeric beads. The large molecules elute first followed by a continuous size spectrum of molecules (de Mora and Harrison 1984).

Direct analysis of a sample by Gel Filtration Chromatography is limited to waters with high metal concentration because the small sample volume compared to eluant gives rise to high dilution factors and large blank values. An alternative approach is to use pre-concentration procedures prior to Gel Filtration Chromatography. This method has been used to distinguish between Cu and Pb size associations with organic materials in coastal waters (Sugai and Healy 1978), although the procedure has unknown effects on metal speciation.

Using Sephadex gels, Gerritze and Salomons (1983) found that in surface waters most of the Cd, Zn and Pb species were in the molecular weight range of 1000-5000. No eluant was found which could elute Cu species from the gels.

Lawson et al. (1984) eluted Cd and Cu sewage sludge species from Sephadex G-25 using 0.05M NaCl (pH 7.0 with NaOH). The technique was applicable when the sludge was spiked with 0.01 mg Cd/l and 0.1 mg Cu/l and showed that Cd was associated with the lower molecular weight fractions while Cu existed as predominantly high molecular weight species.

Gel Filtration Chromatography has also been applied to the speciation of Pb in tap water (de Mora and Harrison 1983a, 1984). Qualitative evidence of large humic complexes and small inorganic/organic Pb complexes (< 1500 molecular weight) was obtained. However, the low recovery efficiencies of 6-50%, due to metal complex resin adsorption, precluded the use of Gel Filtration Chromatography as a quantitative metal speciation method for tapwater samples.

#### 2.4.5 Suitability of Physico-Chemical and Physical Separations for Heavy Metal Speciation Analysis.

Several different approaches have been applied to separating fractions of heavy metals in natural waters. Chelating resins are easy to use and relatively free from contamination. By adjusting the properties of the chelating groups attached to a resin it is possible to remove

those metals which are predominantly bioavailable. The organically associated metals are best extracted by acid digestion or by u.v. irradiation, as ozonolysis and resin uptake are more subject to poor efficiency. Size separation is most satisfactorily achieved by filtration or dialysis techniques, although centrifugation is a viable alternative. Ultrafiltration is a difficult technique with some uncertainty over the precision of size separation, whilst Gel Filtration Chromatography is an interesting technique which still requires further development in relation to metal speciation work.

## 2.5 Physico-Chemical Separation Schemes for the Separation of Heavy Metal Species in the Dissolved Phase.

The formulation of the analytical procedures described in the previous chapters into detailed speciation schemes was first attempted by Batley and Florence (1976a). The use of size separation was incorporated into a comprehensive scheme by Laxen and Harrison (1981a). However, both schemes are detailed and require specialised and lengthy analytical procedures. For polluted waters a simple, fairly rapid evaluation of toxic metal content is required (Florence 1982a).

### 2.5.1 The Speciation Scheme of Batley and Florence (1976a).

Despite the difficulties of separating heavy metal species in the dissolved phase, a scheme for application to seawater has been introduced by Batley and Florence (1976a). This comprehensive scheme is illustrated in Figure 2.5. Labile (pH 4.8) and bound metals are analysed by ASV in the differential pulse mode both before and after the sample is subjected to a number of separation techniques. Labile and bound measurements are made at the following stages:

- a) before treatment
- b) after passage through a Chelex-100 column
- c) after u.v. irradiation
- d) after passage of the u.v. irradiated sample through a Chelex-100 column

Seven metal species are identified from the eight measurements and the scheme has been applied by Batley and Florence (1976a, 1976b) to seawater samples.

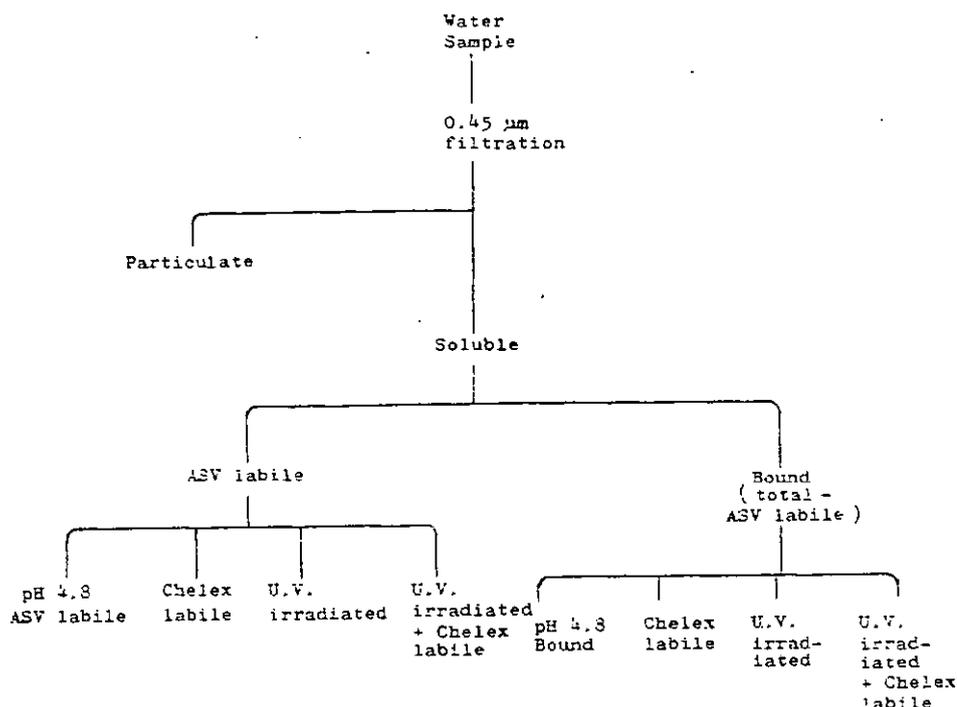


Figure 2.5 Speciation Scheme for Seawater Analysis (from Batley and Florence 1976a).

The results show that, in seawater, Cd is mainly present as ASV labile organic species. Most of the Cu is found to be in the form of organic colloidal complexes but Pb, which forms weaker complexes with organic materials, is mainly present as inorganic colloids.

Batley and Gardner (1978) applied the same scheme to Cu, Pb and Cd speciation in estuarine and coastal waters. Associations of Cd (15-35%) and Pb (45-70%) with inorganic colloids were found to be important, while 40% of Cu was present as inorganic and organic colloids.

In river water the colloidal organic and inorganic species together account for 52% of total Cu, 24% of total Pb and 5% of total Cd (Batley 1983).

#### 2.5.2 The Ultrafiltration Scheme of Laxen and Harrison (1981a).

A scheme incorporating filtration and ultrafiltration as the major separation techniques has been introduced by Laxen and Harrison (1981a) and is illustrated in Figure 2.6. The metal species were size fractionated using Nucleopore filters of 12, 1.0, 0.4, 0.08 and 0.015  $\mu\text{m}$  rated pore size, followed by a series of Amicon ultrafilters. ASV-labile, Chelex-labile and u.v. irradiated fractionations were also included in the scheme. The separation techniques are complex and only a few of the fractions possessed metal levels above the detection limit. However, the ultrafiltration steps gave data on truly dissolved metals which are believed to be highly toxic. In this respect a comparison of the ultrafiltration steps with, for example, bioassays, would be interesting.

The results for the application of this scheme to the effluent from a sewage treatment plant showed that most of the metals were associated with the colloidal and particulate phases (Laxen and Harrison 1981b). However, a high percentage of the Cd (45%) was present in the ultrafilterable, less than 0.015  $\mu\text{m}$ , fraction. Copper is also important in the ultrafilterable fraction (47%) but, although Chelex-labile, it is not present as the ASV-labile form.

In a later application of the scheme to the effluent from a Pb-acid battery manufacturer, the ultrafiltration stage was omitted (Laxen and Harrison 1983), probably because of the problems associated with this technique.

When applied to the speciation of Pb in tap water, this filtration based scheme showed that Pb associates with the whole range of particulate, colloidal and dissolved ligands. Although Pb is often

mostly in the  $< 0.08 \mu\text{m}$  fraction the  $> 12 \mu\text{m}$  fraction can also be important (de Mora and Harrison 1983a, 1983b).

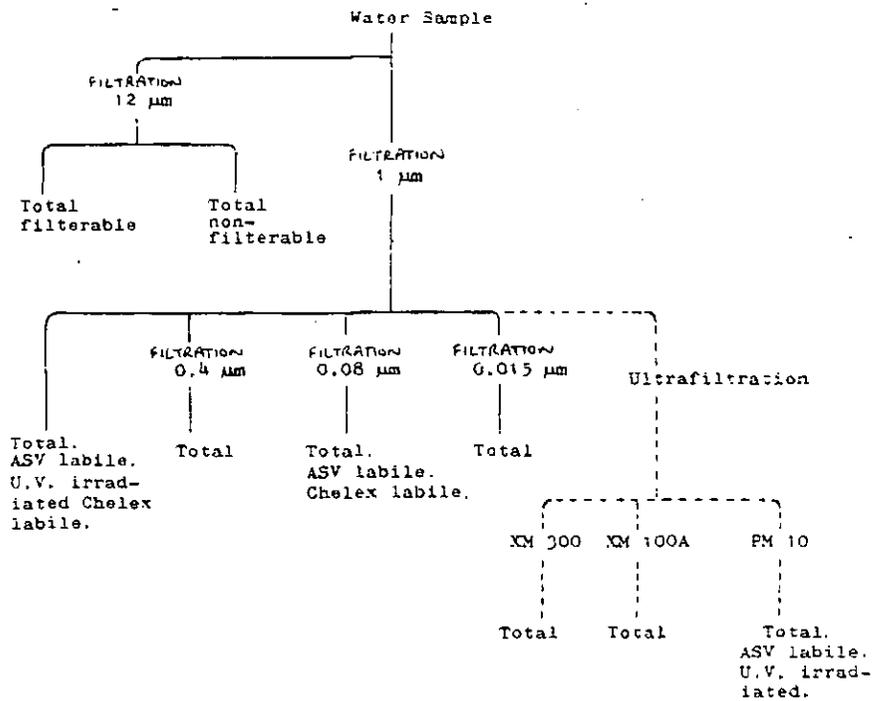


Figure 2.6 Speciation Scheme based on Filtration Separations (from Laxen and Harrison 1981a).

### 2.5.3 Other Speciation Schemes.

The schemes described in 2.5.1 and 2.5.2 require Class-100 clean room facilities, which are designed for the analysis of sub-ppb levels. Another inhibiting factor is their intrinsically detailed nature, leading to an abundance of data which is difficult to interpret. A more satisfactory situation for polluted waters would be a scheme which provides information on the bioavailability, or geochemical mobility, of metals and yet is relatively easy to apply.

The first attempt to devise a scheme for polluted waters was introduced by Stiff (1971). This scheme was designed to assess the

impact of Cu in polluted freshwater and sewage effluents. Free Cu ion, measured by Ion Selective Electrodes, was less than 2 µg/l. CuCO<sub>3</sub> was thought to be an important species on the basis of calculations using uncertain stability constants, total hardness values and free Cu ion concentrations. The species present in the greatest concentration was that described as amino acid complexed, although this fraction probably included any strongly bound species.

Chau and Lum-Shue-Chan (1974) distinguished between labile and non-labile forms of metals in lake water by their response to ASV. Labile metal was determined after the addition of acetate buffer, while bound metals were determined after digestion with persulphate/sulphuric acid or nitric/perchloric acids. A similar differentiation of labile and non-labile species for North Sea and River Rhine samples were carried out by Duinker and Kramer (1977). Zinc was found to be labile, while Cu and Pb were mostly in the bound form. An additional extraction with APDC/MIBK gave the same lability results for Zn, but higher values for Pb and Cu and lower values for Cd.

Relative labilities of metals have been assessed by Figura and McDuffie (1980) in a scheme based on the use of Ca Chelex. Very labile refers to metals which are directly measured by ASV, whereas moderately labile and slowly labile metals are those which are taken up by Ca Chelex column and batch extraction methods, respectively. The inert fraction contains metal which is not susceptible even to Ca Chelex batch uptake and probably represents extremely stable organo-metallic complexes or metal adsorbed strongly to colloidal material. The separations are not completely satisfactory as the very labile fraction is not always fully retained by the Chelex column or batch methods (Batley 1983). Consequently the results cannot be interpreted in terms of dissociation kinetics.

The scheme was applied to river water and most of the Cd and Zn (18-90% and 86-100%, respectively) was found to be present as very labile or moderately labile species. Most of the Pb was associated with the

slowly labile fraction and Cu was almost entirely in the moderately labile and slowly labile fractions.

Hart and Davies (1981) used a combination of Na Chelex (batch method), dialysis and acidification to determine metal speciation in estuarine waters. The determination of other parameters such as chloride, suspended solids and organic carbon, followed by an analysis of this data by a computer simulation, allowed some prediction of the species present.

Cadmium and Zn were fractionated on a column of Chelex by Pik et al. (1982). The remaining metal associations, described as colloidal, were determined by coprecipitation of the metals with a Mo carrier complex. Metal determinations were carried out using the highly sensitive X-ray Fluorescence technique. The results showed that, for estuarine and river waters, Zn was 70-100% Chelex exchangeable, whilst 50-100% of Cu was colloidal.

The importance of the colloidal associations has been shown by Sholkovitz et al. (1978) to be due to the flocculations under estuarine conditions of the 0.1  $\mu\text{m}$  and 0.45  $\mu\text{m}$  size fractions. Welte and Montiel (1980) suggested the use of 0.45  $\mu\text{m}$  and 0.22  $\mu\text{m}$  filtration, to separate these organic colloids, followed by columns of anionic ( $\text{Cl}^-$  form) and cationic ( $\text{H}^+$  form) resins. U.V. irradiation may also be incorporated into the scheme to provide information on organic and inorganic forms.

Dissolved Pb in snow has been found to be mostly present as the cationic colloidal form (Vuorinen 1983). In the same study the particulate phase was also examined and most of the Pb found to be in the 10-60  $\mu\text{m}$  fraction, with 73% readily extractable from the solids by ammonium acetate solution at pH 4.8.

Sugai and Healy (1978) used Gel Filtration Chromatography combined with ASV to identify metal-organic speciation in an anoxic fjord.

Complexation of both Cu and Pb with organic material was observed over a wide range of molecular weights, typically 500-10000.

The concepts of lability and physical separation have been combined by Hasle and Abdullah (1981). Ultrafilterable fractions of coastal seawater were determined by ASV for labile, acid soluble (pH 2.8) and total metals. Acidification releases inorganically and organically complexed metals, whilst organo-metallic compounds probably account for most of the total non-labile fraction. Cadmium and Pb were found to be associated with the low molecular fractions with Cd showing a tendency to be non-labile. Copper was largely associated with organic colloids.

A combination of a speciation scheme and bioassay analyses was used by Ramamoorthy and Morgan (1983) to determine the toxic metal fractions present in wastewater. Metals were separated first by filtration and then by cation and anion exchange resins. The bioassays on *Daphnia magna* and underyearling rainbow trout showed that when metals were removed by the cation exchange resin the toxicity was completely eliminated.

In the same study ultrafiltration was used to show that Zn was mostly in the > 30000 molecular weight fraction, Cd was associated with two lower molecular weight ranges, 1500-10000 (30%) and < 1500 (40%), while Pb was found in the 1500-10000 range (30%) and the > 10000 range (60%).

#### 2.5.4 Assessment of the Techniques and Results from Dissolved Heavy Metal Speciation Schemes.

Speciation schemes for separating dissolved heavy metal fractions have provided some insight into the toxicity and geochemical mobility of metals.

The lability concept applied to ASV and Chelex resin analysis allows some distinction between free and complexed forms (both inorganically

and organically). Physical separation is an additional technique which allows differentiation between colloidal and dissolved metals.

The results for freshwaters generally show that Cd and Zn exist in relatively free forms, Pb is predominantly inorganically complexed, but Cu is found mostly as organic complexes (both colloidal and low molecular weight).

Previous work indicates that the procedures described can be adopted for polluted waters. In such waters the suspended solid phase also becomes an important source of heavy metals.

## 2.6 The Separation of Heavy Metal Fractions in Suspended Solids and Sediments.

Although the toxicity of the dissolved phase is higher because of its direct contact with organisms, the non-lithogenic fractions of suspended solids may subsequently release heavy metals into aqueous systems. The fractions studied must therefore reflect all heavy metal species which might have a direct effect on aquatic biota.

Municipal, industrial and storm surface runoff are increasingly polluting river, marine and estuarine sediments with heavy metals (Gupta and Chen 1975). For instance, the Cd concentrations in the sediments of the river Rhine have increased more than 100 fold in eighty years (Salomons and Forstner 1980). Metal contaminants may exist in relatively unstable forms and may be released by engineering operations such as dredging or by resuspension during storm surges.

It has been reported that pH is probably the single most important factor influencing metal adsorption onto both inorganic and organic surfaces (Forstner and Salomons 1983). This statement however does not consider the importance of changes in ionic strength and measured redox potential, as well as the nature of the surface metal binding sites.

From these considerations several schemes have been proposed for the sequential extraction of chemical fractions from sediments and suspended solids.

#### 2.6.1 Chemical Extractants used in Sequential Extraction Schemes.

The importance of the availability of metals to plants meant that most of the early work was carried out on soils (Jackson 1958). In marine pelagic sediment studies (Chester and Hughes 1967, Nissenbaum 1972) it is the interactions of metal fractions with pore water and the sediment/seawater interface which are of more concern.

The separation of sediment associated metal species into fractions is best achieved by a series of sequential extractions. The extraction steps are not species-selective and repeated treatment often gives a further release of metals, especially in the reducible fractions. They can, however, provide valuable information on the mobility and availability of elements in soils, sediments and sludges (Lum and Edgar 1983).

##### 2.6.1.1 Exchangeable Fraction.

The exchangeable fraction is considered to be that which is available primarily and immediately for biological uptake. It may include metals which are weakly attached to the surfaces of clays or hydrous Fe and Mn oxides or to organic coatings. The addition of a high concentration of chloride or acetate provides a competing ligand for the heavy metals. Hence  $MgCl_2$  (Tessier et al. 1979, Eisenreich et al. 1980),  $BaCl_2$ -triethanolamine (Forstner and Patchineelam 1980) and  $NH_4OAc$  (Salomons and Forstner 1980) have been proposed as extracting agents, usually at 1M concentrations and at pH 7.0. The use of ammonium acetate as an extractant has been criticised due to its tendency to attack carbonates (Tessier et al. 1979).

#### 2.6.1.2 Carbonate Fraction.

Carbonates in sediments exist as cements and coatings which co-precipitate with heavy metals. A lowering of pH, such as occurs with acidified rain, would dissolve carbonates and release the associated heavy metals. The most accepted extraction method is a sodium acetate/ acetic acid (pH 5.0) treatment although some attack on metals weakly bound to hydrous Fe and Mn oxides may occur (Tessier et al. 1979). Forstner and Patchineelam (1980) claim that their acidic cation exchange method is very specific for carbonate associated metals.

#### 2.6.1.3 Hydrous Iron and Manganese Oxide Fraction.

Hydrous Fe and Mn oxides are thought to exist as coatings on particulate surfaces (Davis and Leckie 1978). These coatings have a high capacity for metal adsorption (Gadde and Laitinen 1974). In order to reduce this fraction (Fe(III) to Fe(II), Mn(IV) to Mn(II)), several extractants have been proposed. Dithionite/citrate (Salomons and Forstner 1980), hydroxylamine hydrochloride/acetic acid (Chao 1972, Tessier et al. 1979) and 0.3M HCl (Eisenreich et al. 1980) all appear to have been used successfully

#### 2.6.1.4 Organic Fraction.

Much of the organic fraction will be particle coatings of plant derived organic material. Humic and fulvic acid associated metals can be successfully removed using 1M NaOH. However, the use of sodium hydroxide remobilises metals from phosphates and silicates (Forstner and Patchineelam 1980). Strong oxidising agents, such as 0.4M  $\text{Na}_4\text{P}_2\text{O}_7$  (Eisenreich et al. 1980) may also attack the crystalline phase and so Tessier et al. (1979) decided on a compromise and used an extraction mixture of hydrogen peroxide and 0.02M  $\text{HNO}_3$ . However, metals released from organics by peroxide oxidation are readily adsorbed on clays (Eisenreich et al. 1980).

An alternative and promising approach would be an investigation into various combinations of organic solvents as extractants of the organic fraction, followed by digestion of the released metals.

#### 2.6.2 Evaluation of Sequential Schemes.

Gibbs (1973) distinguished between exchangeable metals, metals attached to metal hydroxide coatings, organic solids and crystalline phases in a study of sediments from the Amazon and Yukon rivers. Forstner and Patchineelam (1980) (Table 2.7) and Tessier et al. (1979) also used sequential schemes to analyse heavy metal fractions in river and estuarine sediments.

The information which these schemes provide is relevant to the ease of metal release to the aqueous phase as well as to processes such as geochemical mobility. There is a certain amount of overlap between the chemical fractions and a scheme with five or six fractions is analytically demanding. It is preferable to devise a scheme, based on established speciation schemes, which will still identify the relevant processes. Hence a less complex sequential scheme has been applied by Salomons and Forstner (1980) to 18 rivers throughout the world. The data, shown in Figure 2.7, shows that metals in polluted waters are mostly associated with the relatively bioavailable fractions (non-lithogeneous) while in unpolluted waters most of the metals tend to be associated with the crystalline fraction. The extraction scheme of Eisenreich et al. (1980), illustrated in Table 2.9, showed similar results in a study of the Mississippi River sediments.

Luoma and Bryan (1981) carried out sequential extractions on a wide range of river sediment samples. The factors affecting trace metal distributions were then analysed statistically. Zinc correlated well with Fe and only weakly with organic carbon, unless the Fe concentration was relatively low. Lead correlated only weakly with both Fe and organic materials, while Cu correlated strongly. Cadmium correlated significantly with Fe, organic carbon and particle size, suggesting that the three are intercorrelated Cd transport mechanisms.

Table 2.7 Sequential Extraction Scheme of Forstner and Patchineelam (1980).

Fractions	Extraction Medium	Interpretation
Soluble	H <sub>2</sub> O	Easily soluble metal
Exchangeable	0.2M BaCl <sub>2</sub> - triethanolamine pH 8.1	Easily extractable fraction (e.g. exchangeable)
Humic and fulvic acid	0.1M NaOH	Metals attached to humic and fulvic acids
Carbonate	Acidic cation exchange	Metals associated with carbonates
Easily reducible	0.1M NH <sub>2</sub> OH.HCl/ 0.01M HNO <sub>3</sub>	Metals bound to Mn-oxides amorphous Fe-oxides
Strongly bound	30% H <sub>2</sub> O <sub>2</sub> + 1M NH <sub>4</sub> OAc	Organic residues and sulphides
Moderately reducible	1M NH <sub>2</sub> OH.HCl + 25% acetic acid	Hydrous Fe-oxide associated metals

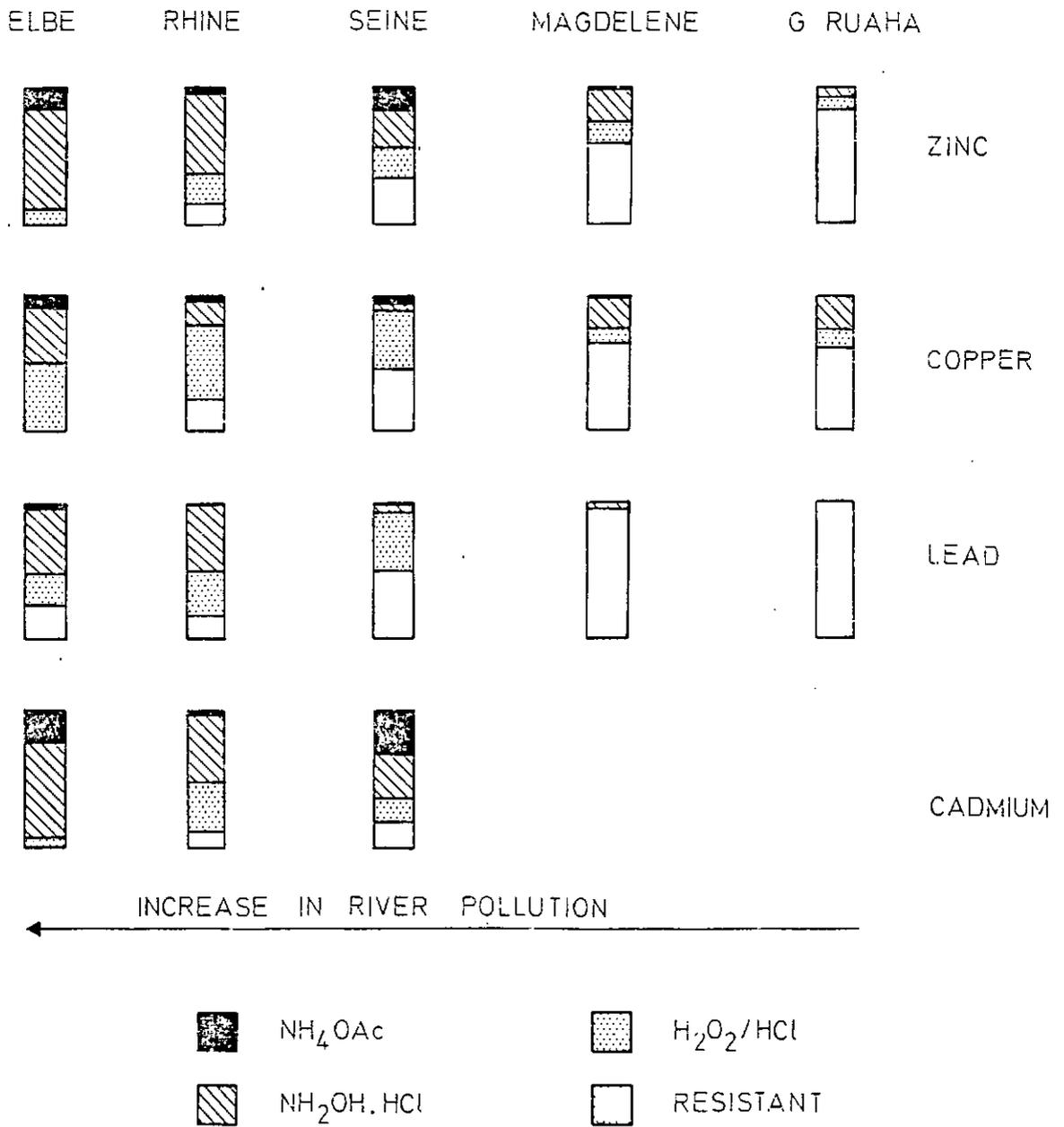


Figure 2.7 Sequential Chemical Extraction Scheme Results for Metals in a range of Polluted and Unpolluted River Sediments (from Salomons and Forstner 1980).

Table 2.8 Sequential Extraction Scheme for Sediments and Suspended Solids (Tessier et al. 1979).

Fractions	Extraction Medium	Interpretation
Exchangeable	1M MgCl <sub>2</sub> , pH 7.0, 1 hour	Weakly adsorbed on clays, hydrous oxides, humic acids
Bound to carbonates	1M NaOAc, pH 5.0 with acetic acid 5 hours	Associated with sedimentary carbonates
Bound to iron and manganese oxides	0.04M NH <sub>2</sub> OH.HCl in 25% (v/v) HOAc 5 hours, 96°C, pH 2.0	Associated with hydrous oxides as nodules, concretions, cement between particles or coatings
Bound to organic matter	30% H <sub>2</sub> O <sub>2</sub> /0.02M HNO <sub>3</sub> , pH 2.0, 5 hours, 85°C, Subsequently NH <sub>4</sub> OAc	Complexed or peptised with natural organic matter, associated with sulphides
Residual	HF/HClO <sub>4</sub> (5:1)	Within the crystalline structure of primary and secondary minerals

Table 2.9 Sequential Scheme of Eisenreich et al. (1980).

Fractions	Extraction Medium	Interpretation
Exchangeable	0.5M MgCl <sub>2</sub> , 7 hours	Adsorbed, ion exchangeable
Organic	0.4M Na <sub>4</sub> P <sub>2</sub> O <sub>7</sub> , 10 hours pH 7.0	Particulate organic coatings
Bound to hydrous oxides	0.3M HCl, 30 minutes, 90°C	Hydrous metal oxide coatings
Residual	Concentrated HNO <sub>3</sub> / HCl/HF	Crystalline bound metals

### 2.6.3 Measurement of Bioavailability of Sediment Bound Metals using In Situ Organisms.

Luoma (1983) has reviewed the uptake of sediment bound metal by detritus feeders and has suggested that the main reason for poor correlations, between sediment bound metal and the concentration of metal in organisms, are the use of a narrow data base. His own studies showed that metal concentrations in a polychaete, *N. diversicolor*, correlated with sediment bound metal concentrations over a wide range of estuarine conditions.

Thomson et al. (1984) determined metal concentrations in the deposit feeding bivalve, *M. balthica*, and found that the bioavailability of Zn contained in sediments derived from urban runoff is lower than in the sediments associated with sewage effluent, discharged to an estuary.

Broberg (1983) compared ETSA (Electron Transport System Activity), which corresponds to bacterial activity, in eutrophic lake surface sediments to added Zn, Cd, Pb and Cu concentrations. At metal levels of 1 to 10 mg/l ETSA decreased in the sediment by 40-90%, with the greatest sensitivity being observed for Cd and Cu. Nitrification experiments showed that metals only slowed, rather than inhibited, oxidation.

At lower metal concentrations bacteria may play an important metal binding role to the sediment surface. Harvey et al. (1982) found a strong relationship between Pb and bacterial enrichment at particulate surfaces in a salt-marsh.

Organisms are obviously useful indicators of metal pollution in sediments. However it must be realised that biological contamination may also be related to poisonous organics or other toxic substances and so organisms provide a more general indication of biological contamination.

#### 2.6.4 The Importance of Determining Heavy Metal Associations in Suspended Solids and Sediments.

Sequential schemes for the analysis of heavy metal speciation in sediments rely on the ease of release of the solid bound heavy metals. This approach is fundamentally different to the dissolved measurements which relate to the complexation strength or lability of the metals.

Comparisons of sequential extraction results, with that metal which is most readily bioavailable, is not straight forward. The most important fraction which can be determined is the exchangeable fraction as this represents the easily released and, therefore, most immediately available metal. Previous studies have shown that this fraction contains higher concentrations in polluted waters where most of the heavy metals are associated with non-crystalline forms. The interpretation of these sequential extraction studies can be greatly

assisted by a consideration of theoretical studies of heavy metal associations with particulates.

## 2.7 Alternative Approaches to Speciation Studies.

Other approaches to speciation studies have been suggested to complement previously reported results and aid in their interpretation. Mathematical models can only be used satisfactorily if enough is known about the major species and their relative stability constants. Particulate surface interactions with metals can be theoretically explained as a result of laboratory experiments. In addition laboratory simulation studies help to explain experimental data from sequential extractions on particulates. Mixing experiments allow some insight into the fate of heavy metals on contact with receiving waters.

### 2.7.1 Mathematical Models.

All the mathematical models presented to date are based on thermodynamic considerations only. If the total concentrations and interactions of all the major components of the aqueous system are known and perfect equilibrium conditions prevail, then the concentration of each chemical species of a given element can be calculated. The values of the stability constants and the corresponding dissolved and surface free ligand concentrations must be known. The uncertainty over many stability constants, particularly with organic ligands, makes a comparison with real data difficult. Another problem is the difficulty of considering all the ligands which may be available in an aqueous sample to complex metals.

In seawater organic ligands are generally present at low levels (1 mg/l) and are therefore thought to be relatively unimportant. This allows calculations on the basis of homogeneous chemical reactions and precipitations, particularly as open ocean water is so well mixed. Hence mathematical modelling of seawater has compared favourably with analytical work (Millero 1974, Whitfield 1975).

In freshwaters two other important interactions must be taken into account:

- a) The adsorption of metals onto particulates (Jenne 1968, Davis and Leckie 1978) and interactions at the suspended solid/water interphase (Westall 1980, Hohl et al. 1980).
- b) The presence of organic material. Most of this material is largely uncharacterised, especially fulvic acids which form important complexes with heavy metals. Organic compounds may be dissolved or present as surface coatings on particulate material (Davis and Leckie 1978).

A computer model, taking these factors into account would need to be backed up by a considerable amount of analytical data. Batley (1983) considers it unlikely that one could ever account for the heterogeneous interaction of metal species with the mixed organic and inorganic colloidal and particulate phases which represent a major component of the total metal concentrations found in most natural systems. Hart and Davies (1981) incorporated data from a speciation study, together with general water quality data, into a computer model. In this way computer calculations were used to assist in the interpretation, rather than prediction, of heavy metal speciation.

#### 2.7.2 Theoretical studies of the Interaction of Heavy Metals with Particulate Fractions.

Interactions between the dissolved, colloidal and particulate phases control the fractionation of heavy metals between each phase. The significant controlling influence of the particulate phase has been recognised for some time (Jenne 1968). However, the heterogeneous nature of particulates in water has slowed down theoretical advances in this field. The distribution of shapes, densities, surface chemical properties and chemical composition may vary widely with size. The sampling process may lead to changes in size and shape (Kavanaugh and Leckie 1980).

Surface exchange theories have been found to apply well to the adsorption of metals on hydrous Fe oxides and residual materials. A theory for the exact behaviour of hydrous Mn oxide does not appear to have been formulated. Organic materials are also capable of complexing heavy metals. These theories are summarised in Table 2.10. From these principles the partitioning of heavy metals between different materials may be more easily interpreted, although component abundance must also be considered.

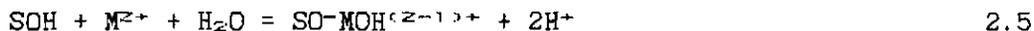
Table 2.10 Control Mechanisms for Heavy Metals in Aquatic Samples.

Control Mechanism	Type of Particulate	Effects on Heavy Metals
Surface exchange	Fe <sub>2</sub> O <sub>3</sub> , silica, alumina, clays	Regulator, a small change in pH may cause significant adsorption or desorption
Co-precipitation, surface exchange	MnO <sub>2</sub>	Removal, an effective sink unless low pH is encountered
Complexation	Organic solids and coatings	Removal, depending on complexation capacity and stability constant

#### 2.7.2.1 Surface Exchange Theory.

Surface exchange theory in natural water systems has been the subject of several publications (Hohl et al. 1980, Westall 1980, Davis and Leckie 1979). Metal ion uptake can be explained by a combination of

surface reactions involving metal ions and their hydrolytic complexes (equations 2.4 and 2.5).



The binding capacity of the surface will be dependent on the specific surface area and the ionic radius of the reacting metal ion (Luoma and Davis 1983). Hence the unhydrated Pb binding capacity for amorphous  $\text{Fe}(\text{OH})_3$  is 22 mmol/g, yet only 1.9 mmol/g for the crystalline goethite.

The James-Healy adsorption model (James and Healy 1973) predicts that at constant pH fractional adsorption should increase with increasing  $\log \beta_1$ , where  $\beta_1$  is the hydrolysis constant for addition of the first -OH to the metal ion (equations 2.6 and 2.7).



$$\beta_1 = \frac{[\text{M}(\text{OH})^+][\text{H}^+]}{[\text{M}^{z+}]} \quad 2.7$$

Consideration of the first hydrolysis constants (Table 2.11) shows that the % adsorption should decrease in the order  $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$ , at a given pH. In fact adsorption of the metal ion begins to occur at a value of  $p\beta_1 = 1.5$  (Gadde and Laitinen 1974, Davis and Leckie 1978, Lion et al. 1982). The values of  $p\beta_1 = 1.5$ , illustrated in Table 2.11, can be compared to the results for metal ion adsorption on hydrous Fe oxides (Figure 2.8). Similar results have been obtained for silica (Huang et al. 1977), clays (Farrah and Pickering 1976a, 1976b, 1977, 1979, 1980) and hydrous Al oxides (Shuman 1977).

Table 2.9 Hydrolysis Constants for Heavy Metal Ions (from Florence and Batley 1980).

	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Zn <sup>2+</sup>	Cd <sup>2+</sup>
First Hydrolysis Constant, pβ <sub>1</sub>	7.0	7.5	8.5	9.5
pβ <sub>1</sub> - 1.5	5.5	6.0	7.0	8.0

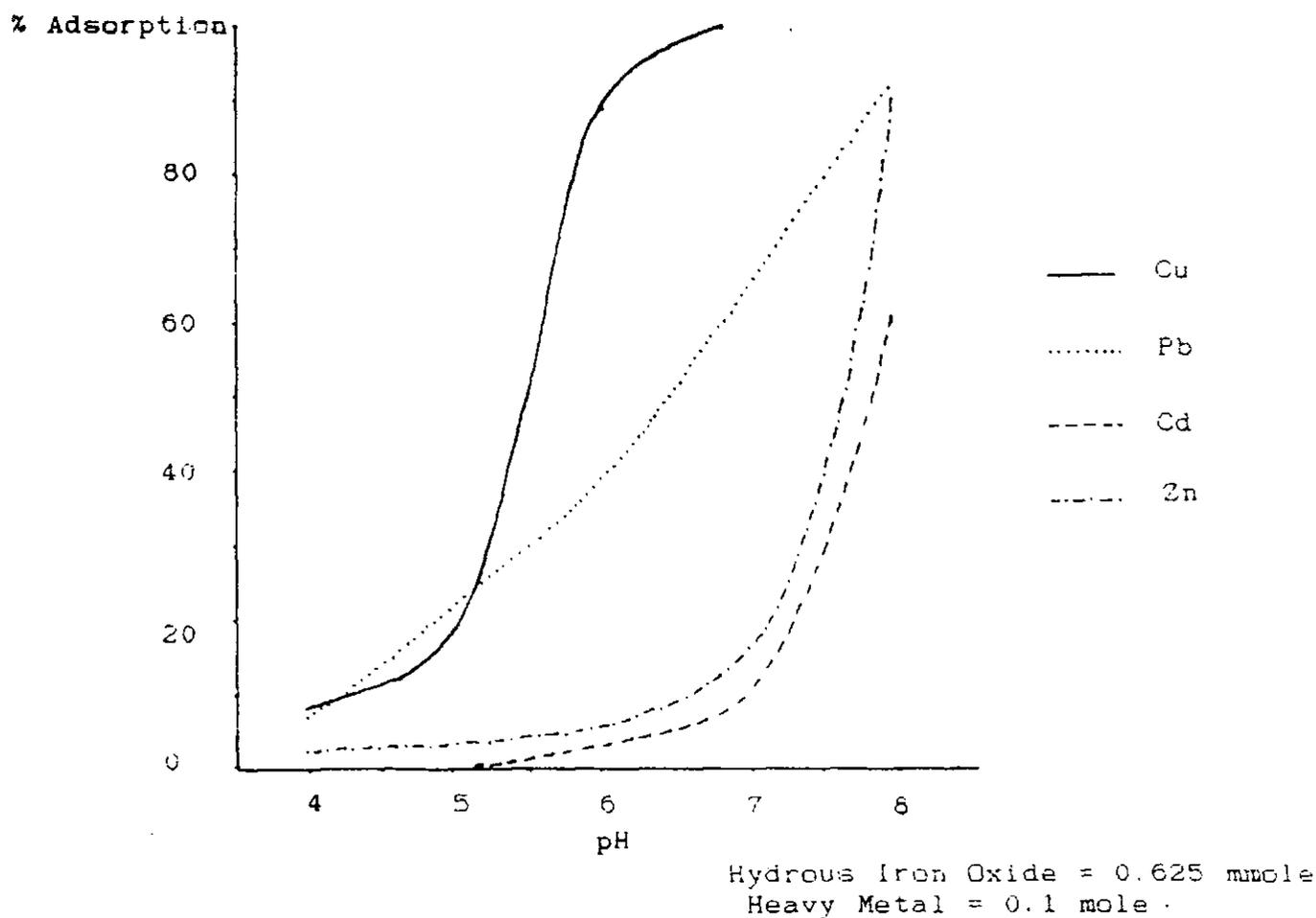


Figure 2.8 Uptake Experiments for Hydrous Fe Oxides (from Davis and Leckie 1978, Gadde and Laitinen 1974)

### 2.7.2.2 The Role of Hydrous Manganese Oxides.

Hydrous Mn oxides show a rather different behaviour to other surfaces, as illustrated in Figure 2.9. Lead is strongly adsorbed, except at very low pH values, whilst Zn and Cd are gradually released with a lowering of pH. Two possible explanations can be given:

a) Consideration of the Zero Point of Charge (ZPC) which has been developed from surface exchange theories because of the importance of surface charge. At pH values higher than the ZPC the surface exhibits an average negative charge and so attracts metal ions. At lower pH values than the ZPC the surface exhibits an average positive charge and so metal ions are repelled. The ZPC for hydrous Mn oxide is 2.8 (Gadde and Laitinen 1974) and this corresponds to the results in Figure 2.9.

b) The surface of hydrous Mn oxides are chemically dynamic, i.e. they are constantly being renewed, added to and changed in oxidation state (Hem 1980). This may mean that the metals associated with hydrous Mn oxide are co-precipitated rather than adsorbed. This explanation can explain the results of Figure 2.9 as metals will remain co-precipitated with the hydrous Mn oxides until the oxides are dissolved and the metals stripped off at low pH values.

Hydrous Manganese Oxide = 0.625 mmole  
Heavy Metal = 0.1 mmole

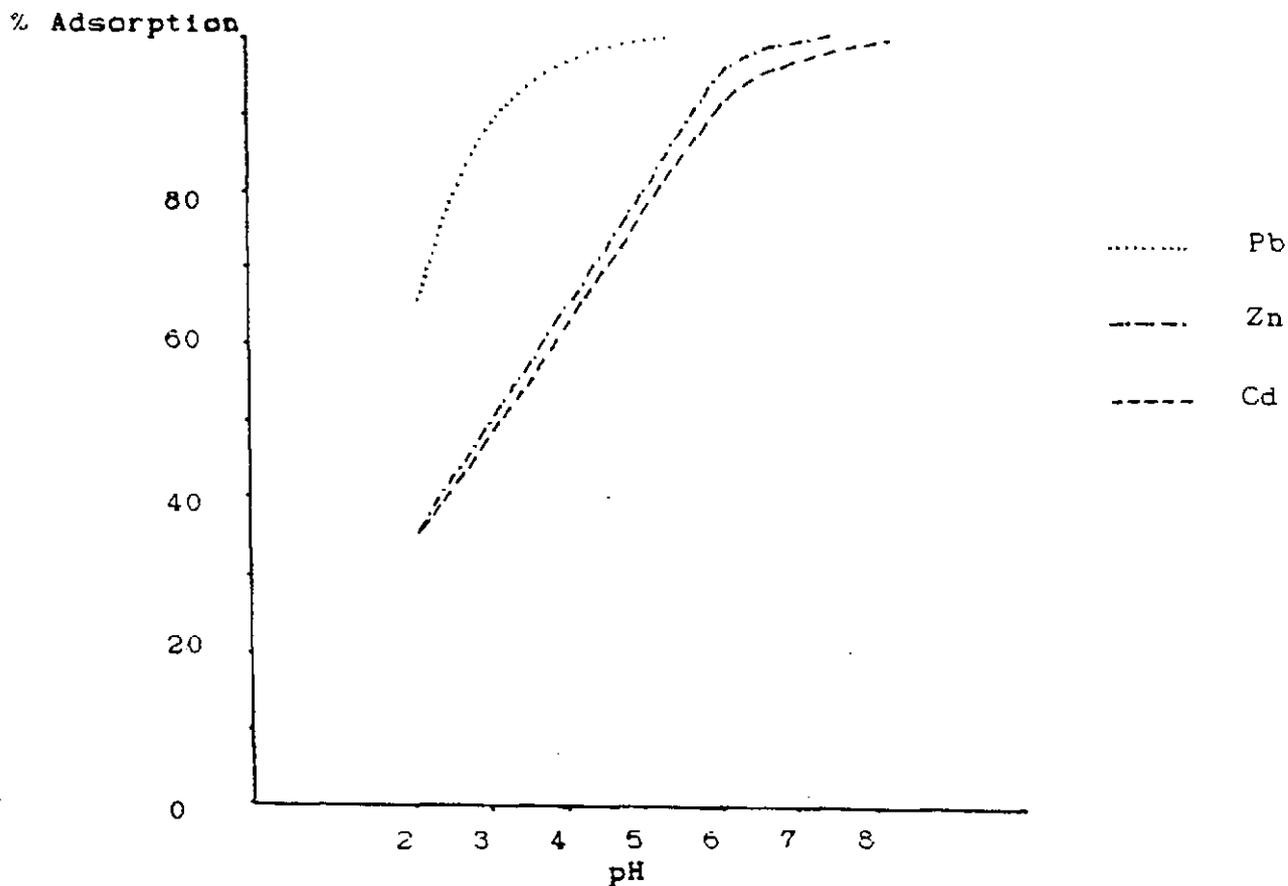


Figure 2.9 Uptake Experiments of Hydrous Manganese Oxides (Gadde and Laitinen 1974).

### 2.7.2.3 Interactions of Heavy Metals with Organic Solids and Coatings.

Organic compounds may form coatings around suspended particles (Davis and Leckie 1978, Lion et al. 1982) or remain as discrete particles. Leppard and Burnison (1983) have described colloidal organic fibrils, largely polysaccharides secreted from algal cells, which also form coatings on particulates.

Certain organic ligands are capable of binding or complexing heavy metals and certainly soil and water derived humic and fulvic acids show this ability (Shuman and Cromer 1979). The complexing ability of organic fibrils is under investigation (Leppard and Burnison 1983). A higher stability constant is found for the complexation of heavy metals with humic substances (i.e. extracted by alkali) at higher pH values (Mantoura et al. 1978).

A comparison of Conditional Stability Constants at pH 8.0 for  $\text{Fe}(\text{OH})_3$  and organics has been made by Luoma and Davis (1983), as shown in Table 2.12. Copper is bound more strongly to organic matter than  $\text{Fe}(\text{OH})_3$  while Cd, Zn and probably Pb are preferentially associated with  $\text{Fe}(\text{OH})_3$ .

Table 2.12 Conditional Stability Constants for Metal Complexation of Amorphous  $\text{Fe}(\text{OH})_3$  and Organic Material at pH 8.0 (from Luoma and Davis 1983).

	log K, pH 8.0 $\text{Fe}(\text{OH})_3$	log K, pH 8.0 Organics
Cu(II)	7.9	8.9-11.4
Pb(II)	9.6	-
Zn(II)	6.7	5.3-5.9
Cd(II)	5.7	4.7

### 2.7.3 Laboratory Simulation Studies of Real Systems.

The laboratory simulation approach is necessarily a simplification of the real system, although it can give some indication of the behaviour of individual components.

Guy et al. (1975) observed the change in heavy metal distribution between various particulate and dissolved components such as hydrous oxides, humic acids and clays, over a wide range of pH values. The model developed as a result of these studies appeared to be in quantitative agreement with reported distributions for natural waters. Typical values for Cu, Cd and Zn are given in Table 2.13. The results show that Cu has a much greater tendency to attach to the particulate phase (represented by MnO<sub>2</sub> and clay) than either Cd or Zn. Copper shows a greater attraction to dissolved humic acids.

Table 2.13 Sorption Characteristics of Humic Acid, MnO<sub>2</sub> and Bentonite (from Guy et al. 1975).

Metal	X <sub>M</sub> (mmol metal/ g MnO <sub>2</sub> )	X <sub>M</sub> (mmol metal/ g humic acid)	Distribution coefficient for clay
Cu	1.95	0.42	9.0
Zn	0.96	0.21	4.3
Cd	1.10	0.22	4.8

X<sub>M</sub> = Maximum sorption values  
pH = 5.0  
Ionic strength = 1.0 × 10<sup>-3</sup>M KAc.

The observed tendency of Cd and Zn to be readily solubilised, in leachate studies on road sediments (Ellis and Revitt 1982), is in agreement with the results of Guy and Chakrabarti (1976) as both metals seem to prefer the dissolved phase.

Laxen (1983) has modelled the behaviour of Cd in freshwaters and suggested that Cd may be bound up in the redox cycling of Fe and Mn because of the importance of hydrous metal oxides. Although the Cd

adsorption to various binding sites was found to be rather dependent on the ionic strength, a relative order of importance for a river suspended sediment was;

Fe<sub>amorphous</sub> > Mn > Clays > Fe<sub>crystalline</sub> > humics > silica

#### 2.7.4 The Product Approach.

Mixing experiments were introduced by Sholkovitz (1976) to determine the composition of removal products (floculants) due to the mixing of filtered river and sea waters at varying salinities. The results of these experiments showed that rapid flocculation of Fe, Mn, Al, P, organic carbon and humic acids occurs in the estuarine environment. Most of the precipitate is formed within one half hour of mixing, and is removed for analysis. A further 24 hours is required before enough precipitate forms for a second determination. The procedure is illustrated in Figure 2.10.

Further studies (Boyle et al. 1977, Sholkovitz et al. 1978) demonstrated the important role of dissolved organic matter. The high molecular weight component of dissolved humic acids (0.1  $\mu\text{m}$  - 0.45  $\mu\text{m}$  filtered) which constitutes a small fraction of river dissolved organic material, is preferentially and rapidly flocculated during estuarine mixing.

The application of mixing experiments to the modelling of the impact of stormwater on river water would be interesting. During winter storms high concentrations of chlorides are frequently observed due to the use of de-icing salt. The resulting large change in ionic strength between incoming stormwater and ambient river water may give rise to changes in the speciation of the toxic metals. Other parameters which are often significantly different between stormwater and river water, and which may result in flocculation, include pH, organic material (both dissolved and particulate), suspended solids loadings and Fe and Mn concentrations.

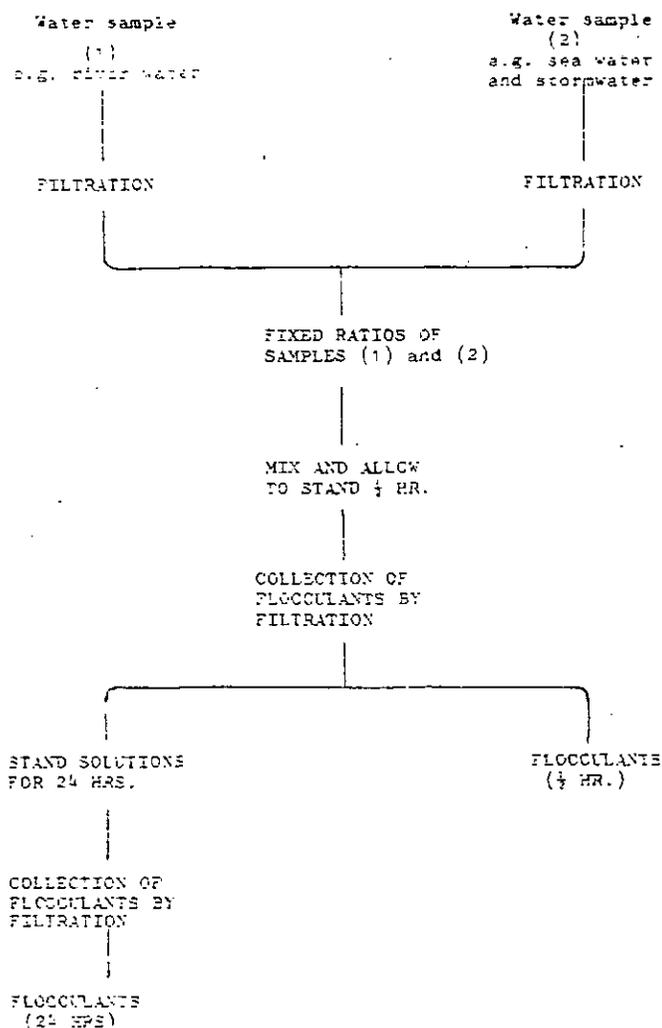


Figure 2.10 Procedure for Mixing Experiments (from Sholkovitz 1976).

### 2.7.5 The Relevance of Theoretical Studies of Heavy Metals in Natural Waters.

A comparison of theoretical studies with the data from speciation schemes shows that some similarities exist between the two approaches. Copper is found mostly in the organic fraction of particulates because of the high stability of the resulting complexes; for the same reason

Pb is mostly associated with hydrous metal oxides. Zinc and Cd tend to be more readily solubilised in the pH range of most aquatic samples.

Mathematical models, theoretical studies, laboratory simulation and mixing experiments are useful methods for interpreting heavy metal fractionation data from speciation schemes.

## 2.8 Apparent Heavy Metal Complexing Capacities and Conditional Stability Constants in the Aqueous Environment.

Organic ligands of both simple and complex structure occur in abundance in natural waters, typically at concentrations of 10 mg/l in river water. Approximately half of these organics are fulvic acids (Saar and Weber 1982), which closely resemble organic extracts from soil (Reuter and Perdue 1977).

A large proportion of heavy metals in natural waters are believed to exist in complexed or chelated forms with organic ligands (natural or anthropogenic) which therefore act as regulators of metal availability (Chau 1973). Complexation may therefore control the geochemical transport and bioavailability of metals in the aquatic environment (Van den Berg and Kramer 1979a).

In addition to increasing the possibility of heavy metal transport in natural waters, as well as through wastewater treatment processes, complexing agents may hinder the removal of metals from water, increase the corrosion of metal surfaces and affect the oxidation state of metals in water (Kunkel and Manahan 1973).

Analysis of the complexation properties of these organic compounds is complicated by the irregular structure and wide range of components present. Several experimental methods have been developed to investigate the complexing behaviour of organic fractions in natural waters. Most methods involve a titrimetric procedure in which the ligands are reacted with a suitable metal ion until the end point, equivalent to the complexing capacity, is reached. A technique to

detect remaining free metal is therefore required. Voltammetry is the most tested method (Shuman and Woodward 1973, 1977, Shuman and Cromer 1979) although it may measure weakly complexed metals in addition to free metal ion. Potentiometry, Ion Selective Electrodes, solubilisation, bioassay and ion exchange are other available techniques.

#### 2.8.1 Polarography and Voltammetry.

Preliminary polarographic studies of consecutively formed complex ions (Deford and Hume 1953) were developed by Matson (1968) who used ASV as a sensitive technique to detect free, as opposed to organically complexed, Cu. Copper is a satisfactory metal for the titration as it forms strong, specific complexes with many organic compounds.

Methods for determining Apparent Complexing Capacity (Chau 1973, Chau and Lum-Shue-Chan 1974) and later Conditional Stability Constants (Shuman and Woodward 1973, 1977) have since been developed. The method is rapid, sensitive, allows the determination of total ligand concentration and is applicable over a wide pH range.

##### 2.8.1.1 Determination of Apparent Complexing Capacity.

The technique is essentially a complexometric titration of metal ion against ligand. Where ligands are titrated sequentially, those with the highest stability constants are complexed first of all (Crosser and Allen 1977).

A typical titration curve for Cu with a water sample is illustrated in Figure 2.11. When ligands are present, and their individual concentrations are small, a smooth curve, as shown by the dashed line in the figure, is typical. In this case the sharp changes in stability constants are offset by small changes in concentration. Changes in titration slope are therefore related to the product of the concentration of the ligand times its Conditional Stability Constant.

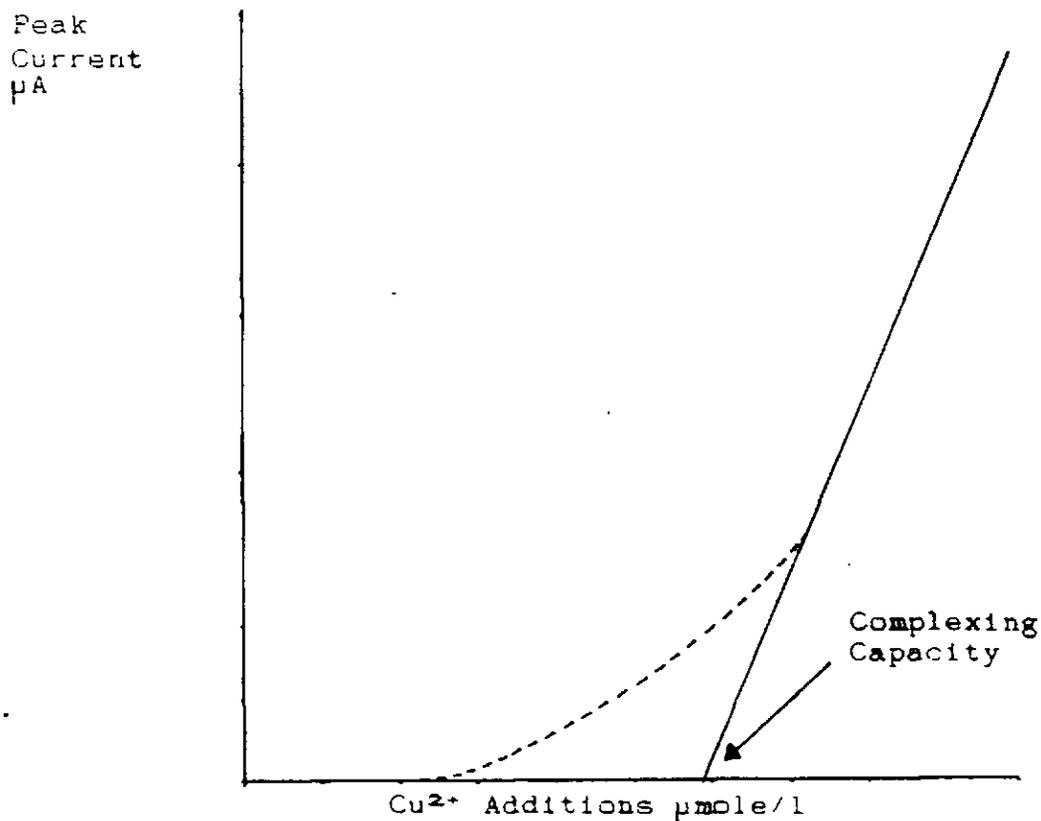
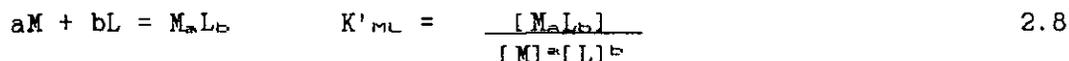


Figure 2.11 Theoretical Titration of a Water Sample with Copper.

The Apparent Complexing Capacity is found by extrapolation of the free metal ion (final slope) to the x-axis. There appears to have been some ambiguity in the literature regarding this determination. Some authors have used the value of  $C_{0.1}$ , which is the value at the point of inflection of the final and the directly preceding slopes (Dwinker and Kramer 1977, Hart 1981, Shuman and Woodward 1977). This value is then used in the calculation of Conditional Stability Constants. Other authors (Eisenreich et al. 1980, Laxen and Harrison 1981b, 1983) appear to have used the recommended procedure of Chau (1973) as illustrated in Figure 2.11.

### 2.8.1.2 Calculation of the Conditional Stability Constant.

The Conditional Stability Constant can be calculated on the basis of formation of the complex (equation 2.8):



where a and b depend on stoichiometry

L = Ligand

M = Metal

K'\_{ML} = Stability Constant

For a given Complexation Capacity, the initial slope becomes lower for increasing values of the Conditional Stability Constant. Using ASV titration data, Shuman and Woodward (1973, 1977) derived equation 2.9:

$$i_{\infty} \equiv \frac{k}{(K'_{ML})^{1/a}} \cdot \frac{(C_M/a)^{1/a}}{(C_L - b/a C_M)^{b/a}} \quad 2.9$$

where  $i_{\infty}/k$  = slope of graph after all complexing sites are filled

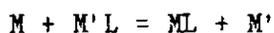
$C_M$  = concentration of metal added

$C_L$  = concentration of total ligand at the intercept

For a 1:1 complex a plot of  $i_{\infty}$  vs  $[C_M/(C_L - C_M)]$  has a slope of  $k/K'_{ML}$  while for a 1:2 complex a plot of  $i_{\infty}$  vs  $C_M/(C_L - 2C_M)^2$  has a slope of  $k/K'_{ML}$ .

With low stability constants the calculation is accurate, within 20%, for titration values up to halfway to the endpoint ( $C_L$ ). The error decreases for higher Stability Constants. Some kinetic dissociation has been observed for humic and fulvic acids (Shuman and Cromer 1979) and the extent is dependent on ligand concentration. After applying a suitable correction factor the Stability Constant was not significantly changed, while the Complexation Capacity was slightly increased.

In environmental samples displacement reactions can take place in addition to the direct reaction in equation 2.10 (Neubecker and Allen 1983).



$$K'_{ML} = \frac{[ML][M']}{[M][M'L]}$$

2.10

where M' = a different metal

Therefore, the conditions for measurement, e.g. pH, ionic strength and competing complexation, are different from those relevant to the determination of the Thermodynamic Stability Constant and the term Conditional Stability Constant is used. The changes in the Conditional Stability Constant during titration may be offset by small changes in concentration and hence it may only be possible to quote an Average Conditional Stability Constant for a plethora of ligands.

Although the results depend on the experimental conditions the technique is simple and straightforward to carry out. Some workers have found problems with the use of ASV as the measurement technique in that metal complexes may be reduced by the electrochemical procedure. This problem can be overcome by operating at potentials only high enough to reduce the free metal ion. Another area of concern is that surface active organic material may be adsorbed to the electrode surface causing erroneous free metal values.

The use of this method has been criticised by Tuschall and Brezonik (1981) and shown to give low stability constant values compared to other methods. The subject remains controversial as is indicated by an exchange of comments by workers in the field (Bhat and Weber/Tuschall and Brezonik 1982).

### 2.8.2 Other Methods.

Potentiometric titration has been widely used by soil scientists (Schnitzer and Kahan 1972) for determining the Complexing Capacity of isolated materials. As a direct technique an insufficient change of pH is found in natural waters due to the low concentrations of complexing ligands and the high concentration of bicarbonate. Shuman and Cromer (1979) carried out a potentiometric titration on humic and fulvic acids isolated from lake water. The Cu Complexation Capacity from ASV

titration data only represented 15% of the theoretical capacity from total acidity.

Ion Selective Electrodes, in theory, only measure free ion and should therefore be very suitable. However, it is generally difficult to achieve Nernstian response below a filterable Cu concentration of 1  $\mu\text{M}$ . Buffle et al (1977) have applied the technique to freshwaters, but difficulties arise in obtaining a stable response, probably due to the presence of organic ligands.

Solubilisation finds most application when studying strong chelating agents such as EDTA. The procedure, introduced by Kunkel and Manahan (1973), is based on the solubilisation of metal by the addition of ligands to a metal hydroxide suspension at pH 10.0. The precipitate is filtered and soluble Cu determined by Atomic Absorption

Spectrophotometry. A concentration of Cu in the filtrate greater than 15  $\mu\text{g/l}$  must be due to complexation by water sample constituents (under the conditions of the experiment). Despite the simplicity of the technique there are many problems including:

- a) the requirement of highly alkaline pH conditions (Campbell et al. 1977).
- b) incorrect results are obtained with weak ligands (Frimmel et al. 1980).
- c) the necessity of boiling the solution for one hour (Neubecker and Allen 1983).
- d) the slow attainment of equilibrium between the solution and the precipitate, precipitate ageing and the operational definition of solubility in terms of filtration through a 0.45  $\mu\text{m}$  filter (Crosser and Allen 1977).

Biological response or bioassay is related to the response of micro-organisms (Davey et al. 1973) to the toxic forms of heavy metals. By measuring a metabolic parameter as a function of added Cu ion, the fraction of bioavailable (free Cu in solution) can be determined. A titration-like curve may be formed from which an endpoint is estimated (Davey et al. 1973, Gatcher et al. 1978, Gillespie and Vacarro 1978).

Ion exchange, introduced by Schubert (1948), has been well tested by soil scientists (Zunino et al. 1972, Schnitzer and Kahn 1972) although the ion exchanger tends to strip the metal from its complexes. The ion exchanger behaves as a second ligand onto which the metal can become bound.

A more acceptable technique, utilising a weak ion exchanger,  $MnO_2$ , in place of synthetic resins has been introduced by Van den Berg and Kramer (1979b). Most free Cu ion is bound and the hydrous oxide does not remove metals from complexes. The method works well for complexes with Conditional Stability Constants lower than  $\log K = 10$  and also for low ligand concentration (0.2 mg/l organic C). The formation of ternary complexes of organic ligands at the oxide surface (Davis and Leckie 1978) is the main criticism of this technique.

#### 2.8.3 Comparison of Methods.

Sterritt and Lester (1984a) have compared the Conditional Stability Constants obtained for Cd, Pb and Cu with fulvic acid by using three different analytical techniques; Ion Selective Electrodes, dialysis and ASV. The stability constants obtained by ASV measurements were lower than for the other two methods, suggesting the existence of increased metal complex lability. However, the Complexation Capacity was similar for all methods. Ion Selective Electrodes detected both weak and strong complexes, while ASV and dialysis were only sensitive to stronger complexes. For stronger complexes a  $\log K$  range of 4.7 to 7.0 was found, while weaker complexes gave a  $\log K$  value of between 3.8 and 5.6 for all three metals. Weaker binding sites often show a much greater metal capacity for Cu and Cd than stronger binding sites (Sterritt et al. 1984b, Sterritt and Lester 1985).

#### 2.8.4 Application and Interpretation of Heavy Metal Complexing Measurements.

There is still a certain amount of critical discussion regarding the measurement of heavy metal Complexation Capacity and the presently

available techniques require further development. However, the importance of the ability of organic ligands to complex heavy metals is well recognised. For this reason the ASV titration method, if standardised with respect to analytical conditions, is a simple technique for monitoring the spatial and temporal variations of complexing organic ligands in polluted waters.

## 2.9 Clean Methods and Problems of Trace Analysis.

The maintenance of consistently low blank values is difficult at trace levels. Many of the contamination problems concerning the sampling and storage of water samples, for heavy metal analysis, were not solved until the mid-1970's (Batley and Gardner 1977). The control over contamination depends on good laboratory practice (Kosta 1982). Contamination can occur at any stage of the analytical procedure, although sampling and sample preparation seem to be the most critical steps.

### 2.9.1 Sampling.

The sample containers should preferably be of polyethylene and be washed before use in a 10% HNO<sub>3</sub> bath for 24 hours. After rinsing thoroughly with purified water the sample can be taken or the bottle placed in the sampler. For heavy metal speciation studies the sample must be filtered on the day of collection due to the danger of sample changes. The rapid loss of metals by precipitation or adsorption on container surfaces can be a major problem during sample storage (Harrison 1983).

### 2.9.2 Laboratory Atmosphere.

The fallout of heavy metals in dust particles is typically 0.01-0.1 ng/cm/day for a laboratory (Kosta 1982). This can be reduced by 10-100 times in a dust free room. Dust and particles from the activities of

personnel are the greatest source of contamination. Dirt particles from shoes can be captured by a sticky floor covering (Mart 1982). Where the sample is likely to be exposed for a long time period, or for samples with low metal concentrations ( $< 1 \mu\text{g/l}$ ), a laminar flow hood is required to prevent gross contamination. To prevent cross-contamination, preparation steps which involve concentrated chemicals should be excluded from the working area used for metal determinations.

### 2.9.3 Laboratory Ware.

Materials which are typically used in a laboratory include polyethylene, polypropylene, rubber, Teflon, glass and silica. Some materials, such as rubber, can contaminate a sample, while some, such as glass, can adsorb metals from a sample (Batley and Gardner 1977).

Table 2.12 shows the levels of metals in certain laboratory materials. Polyethylene is usually the recommended material for trace metal work, as it is possible to remove most of the plastic matrix associated metal, which is high in Zn and Pb, by soaking for 48 hours in a 10%  $\text{HNO}_3$  bath (Laxen and Harrison(1981a). Metal species are not adsorbed to a significant extent to the polyethylene surface when samples are stored at neutral pH values, while the Pb content of acidified samples (pH 2.0) only increases by 1 ng/l every two weeks (Mart 1982).

Polyvinyl chloride (PVC) contains Zn, Cd and Pb at the 0.1-10 mg/Kg concentration which is due to their use as stabilisers during manufacture. Teflon is an excellent material for metal samples, but is too expensive for routine work. Polycarbonate, glass and silica are not suitable for sample storage as they adsorb metals to their surfaces. However, glass can be used for the routine digestion of acidified samples, after acid cleaning.

Table 2.12 Typical Metal Levels in different Laboratory Materials  
(from Kosta 1982, Heydorn and Damsgaard 1982).

	mg/Kg		
	0.1-10	0.01-0.1	0.001-0.01
Polyethylene and polypropylene	Zn, Pb	Cd	Cu
PVC	Zn, Cd, Pb		
Teflon		Cu	
Polycarbonate		Pb, Cu	
Glass	Zn, Pb, Cu		
Silica		Cu	Cd

#### 2.9.4 Laboratory Reagents.

Ultra-pure water can be obtained from a Milli-Q ion exchange system when it is fed with double distilled water. Typically the following low blanks are obtained from the system, Cd < 0.1 ng/l, Pb < 2 ng/l, Cu < 10 ng/l (Mart 1982). No data was given in the latter reference for Zn.

High purity acids can be obtained from BDH (U.K.) or Merck (W. Germany). Usually the trace metal levels are ten times lower than the label indicates, with Cu and Zn typically quoted at between 5 and 50 µg/l (Kosta 1982). If required these levels can be reduced by 100-1000 times by the use of a sub-boiling point still. However, when acidifying samples to pH 2-3 (typically 50 µl high purity acid/50 ml sample) only 0.3 ng/l Pb is added (Mart 1982).

Other reagents may contain variable amounts of metals and may be difficult to purify. It is therefore important to obtain the highest purity reagents available and to check their blank addition during use. If further purification of reagents is required then this can be achieved by controlled potential electrolysis, solvent extraction or ion exchange (Batley and Gardner 1977).

### CHAPTER 3 CATCHMENT CHARACTERISTICS AND INSTRUMENTATION.

Stormwater concentrations and loadings of heavy metal species were studied at the stormwater outflow pipe of two urban catchments. One residential catchment was chosen in England and one in Sweden; both catchments are housing areas developed for population overspill during the 1950-1970 period. For a smaller scale study, in an attempt to provide a mass balance for heavy metal species in an urban area, a parking lot at Chalmers University of Technology, Gothenburg, Sweden, was selected. Only the area draining into a single gullypot was considered in this latter case.

The catchments used were:

- a) Oxhey; a 247 hectare residential estate on the north west fringes of Greater London, England.
- b) Bergsjön; a 15.6 hectare residential estate in the north eastern suburbs of Gothenburg, Sweden.
- c) Chalmers; a 390 m<sup>2</sup> car parking lot on the site of Chalmers University of Technology, Gothenburg, Sweden.

#### 3.1 The Oxhey Catchment.

The Oxhey housing estate is predominantly composed of semi-detached and terraced houses built during the 1950's, with further re-development during the period 1965-1975. The development also includes grass verges, gardens and open spaces, a small shopping precinct, schools as well as other public buildings and a car park (Figure 3.1).

A long throated trapezoidal flume was constructed in 1952 at the catchment outfall by the Transport and Road Research Laboratory (TRRL), U.K., for the purpose of developing suitable procedures for stormwater sewer design. It was subsequently used by Wilkinson (1956) to determine patterns of pollutant discharge, and by Harrop (1984) for more intensive stormwater runoff quality studies.

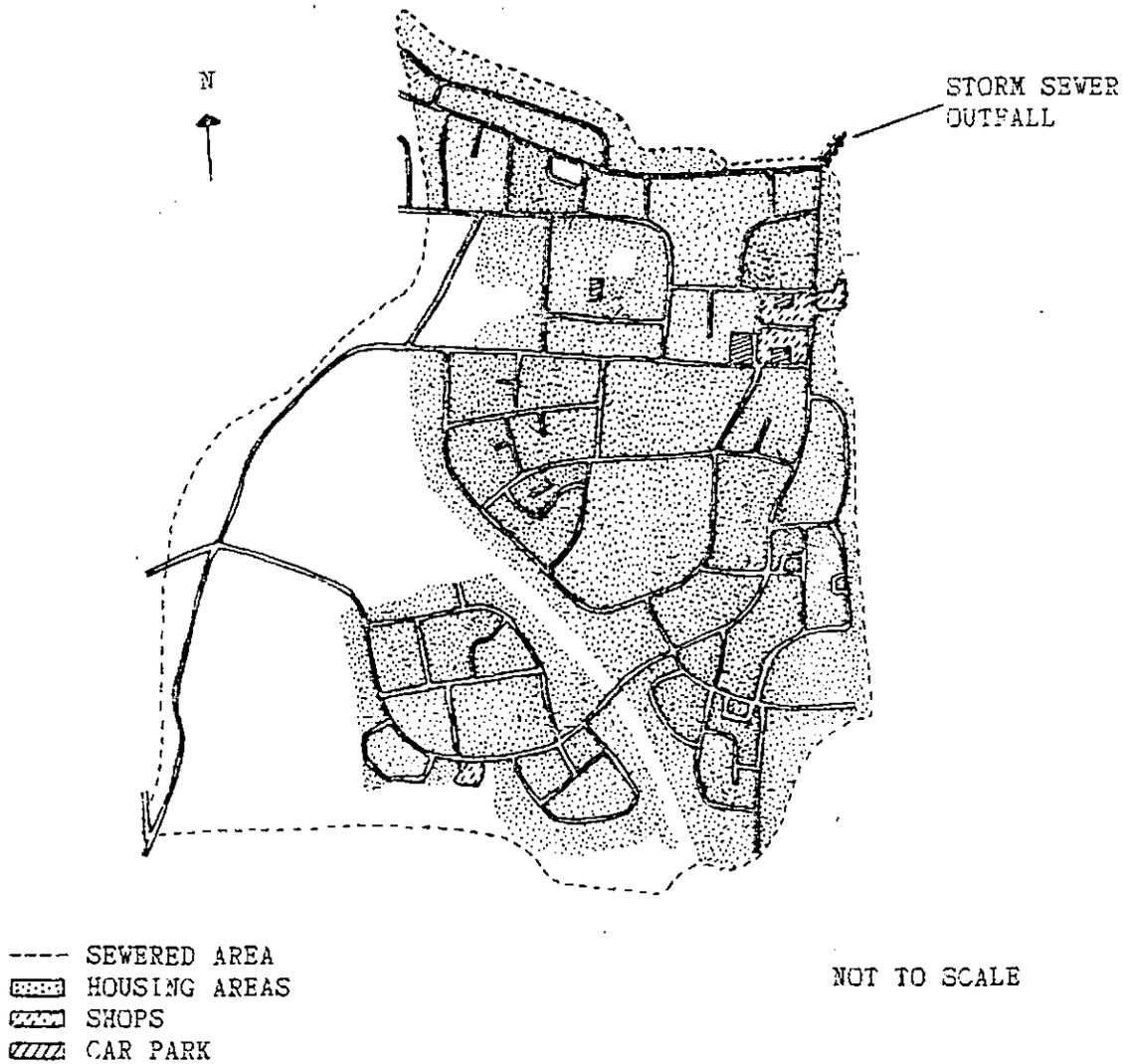


Figure 3.1 Sewered Contributing Areas on the Oxhey Catchment.

3.1.1 Catchment Characteristics.

The prime characteristics of the catchment are given in Table 3.1. Both Wilkinson (1956) and Harrop (1984) have noted high concentrations of Biological Oxygen Demand and suspended solids occurring during the first 30 minutes of runoff which is twice as polluted as the rest of the flow. However, a prolonged attenuation of turbidity is found after the time of concentration has been exceeded.

Table 3.1 Characteristics of the Oxhey Catchment.

---

Area (ha.)	247
% Impervious Area	19.8
% Average Slope	2.3
Depression Storage Value (mm)	2.17
Time of Concentration (min)	19.2

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### 3.1.2 Flow Measurements.

The surface water from the catchment is drained via the separate storm sewer pipes to the Hertsbourne River and eventually into the River Colne.

The depth of flow through the flume, prior to discharge to the receiving stream, is measured with a level float installed in a separate stilling well. In 1952, the TRRL calibrated the flow volume against stage height and Harrop (1984) has described the resultant rating curve by two equations (equations 3.1 and 3.2).

$$Q = 1.4 + 0.53h + 5.66 \times 10^{-3}h^2 - 3.64 \times 10^{-6}h^3 + 1.10 \times 10^{-9}h^4$$

(flow > 10 l/s) 3.1

$$Q = 0.465h^{1.279}$$

(flow < 10 l/s) 3.2

Q = Flow (l/s), h = Stage height (mm)

Stage height data is recorded at one minute intervals on a cassette tape using a Microdata M200L data recording logger

### 3.1.3 Sampling.

Sampling is achieved through a caged intake positioned in the throat of the flume and which is fully immersed during storm flows. Samples are drawn through a 12 mm plastic pipe with an overall head height of 10 metres. Sampling is activated when the water reaches a flow volume of 91 l/s. At this point microswitches close the power supply circuit on an automatic Rock and Taylor 48 bottle sampler. Sequential continuous samples are withdrawn over a five to eight minute period at approximately 150 ml/min. Collected samples were returned to the laboratory on the day of sampling and subjected to the analytical procedures outlined in Chapter 4.

### 3.2 The Bergsjön Catchment.

Bergsjön is a smaller catchment than Oxhey, but also constructed for the purpose of housing central city overspill population during the 1960's. The area contains nine blocks of multi-storey buildings, two open parking lots and a shopping centre (Figure 3.2). The hydrology of the catchment has been described in detail by Arnell (1980, 1982) and metal/nutrient loads in the storm runoff are discussed by Malmqvist (1983).

#### 3.2.1 Catchment Characteristics.

The prime characteristics of Bergsjön are shown in Table 3.2.

Table 3.2 Characteristics of the Bergsjön Catchment.

Area (ha.)	15.6
% Impervious Area	39.1
Area of Catchment with Cu Surfaces (m <sup>2</sup> )	1700
Area of Catchment with Zn Surfaces (m <sup>2</sup> )	1190
Depression Storage Value (mm)	0.42
Time of Concentration (min)	6

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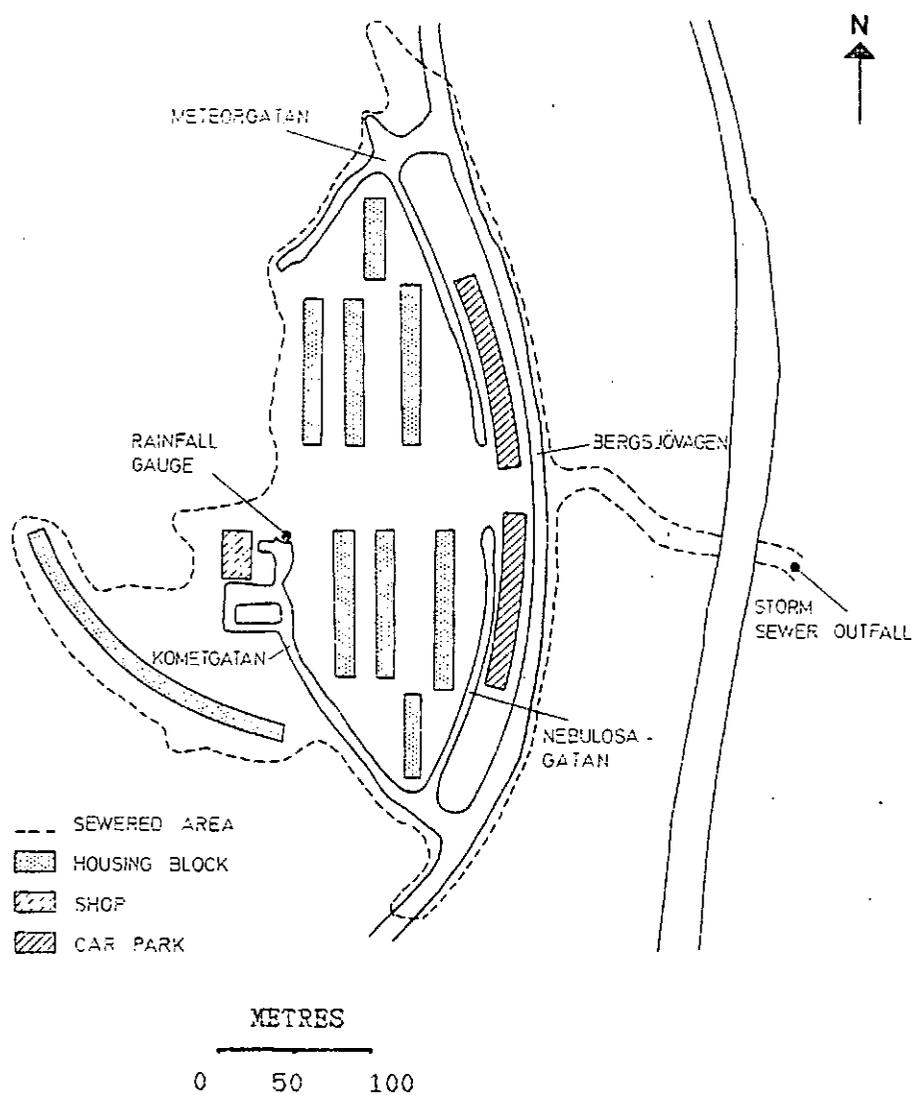


Figure 3.2 Sewered Contributing Areas on the Bergsjön Catchment.

There is a great deal of Cu and Zn surfacing within the catchment, the former being extensively used for guttering and the latter for street furniture.

### 3.2.2 Flow Measurements.

The depth of the stormwater flow at the sewer outfall is measured across a sharp crested 120° V-notch weir, using an ultra-sonic level detector (Figure 3.3). Flow has been calibrated against stage height by isotope measurements to give equation 3.3.

$$Q = 4.09h^{2.5}(0.6 + 0.25h^{1.5}) \quad 3.3$$

Q = Water Flow (m<sup>3</sup>/s), h = Water Level (m).

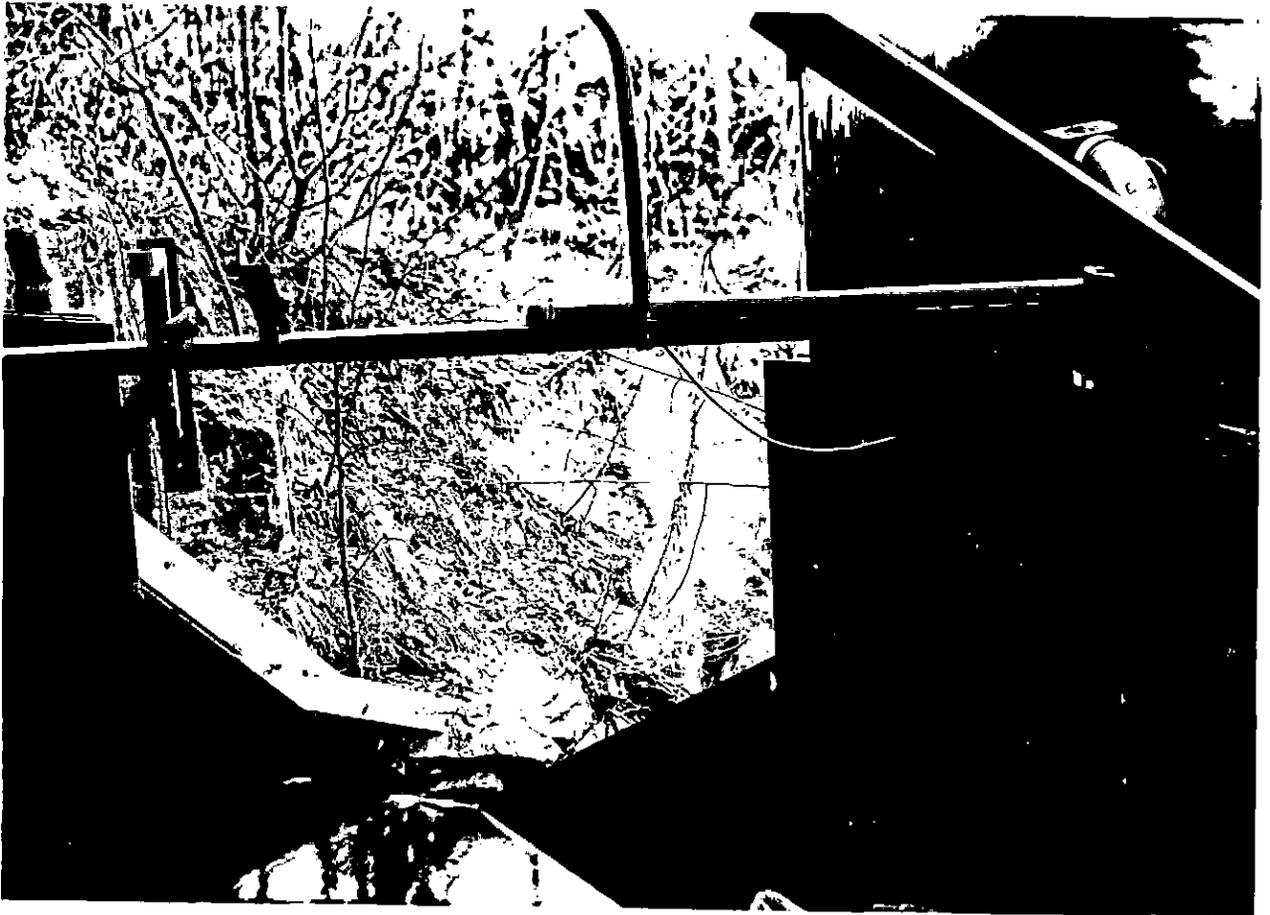


Figure 3.3 Secondary Flume for Monitoring Flow at the Bergsjön Field Station.

The stage height is recorded on a chart recorder and, after conversion to flow volume, is stored in digital form.

### 3.2.3 Rainfall Measurements.

A rainfall gauge of the siphon type is situated in the catchment (Malmqvist 1983) and provides continuous data on an internal chart recorder.

### 3.2.4 Continuous Pollutant Monitoring at Bergsjön.

Water is continuously pumped into the Bergsjön outfall field station, through a 20 mm PVC pipe, by a Johnson F5B-1 Impellor pump, at a rate of 34 l/min (Figure 3.4). After passing through a sampling header tank the water flows into the continuous pollutant monitoring system (Figure 3.5).

The continuous flow system is constructed from a sealed PVC pipe and holes in the upper surface allow the insertion of a series of sensors, which include a conductivity electrode, a temperature sensor and a pH electrode. Turbidity is measured externally in the stormwater pipe, by a photo-electric cell. The electrode signals are recorded both on a Chino 12 channel chart recorder and in a digital form utilising an ABC 80 microcomputer.

A typical storm profile from the Bergsjön stormwater sewer system is shown in Figure 3.6. An increase in the incoming flow is followed immediately by changes in conductivity. This indicates dilution of the baseflow, which usually contains 100-200 mg Cl/l, by the incoming rainfall and runoff. On the recessional limb of the storm event the higher baseflow conductivity level is re-established.

The change in pH is slower and does not represent the incoming rainfall pH, which is typically ca. 4.0. During storm events buffering can be attributed to the washing of road surfaces and the flushing of gullypots within the catchment. In addition it is thought that the

dissolution of cement in the concrete pipe network is an important source of bicarbonate ions. The contact time of rainfall-runoff with the rather large surface area of the storm sewer pipes may be up to six minutes between the catchment and the end of pipe.



Figure 3.4 Water Sampling at the Bergsjön Field Station.

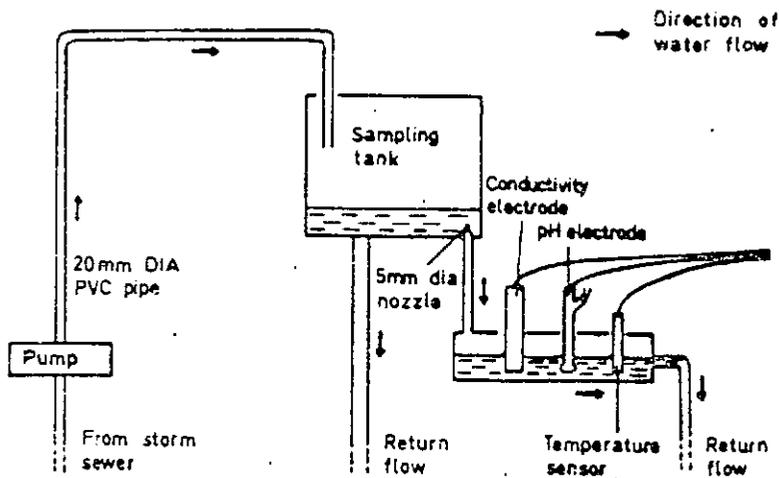


Figure 3.5 The Continuous Monitoring System inside the Bergsjön Field Station.

Changes in turbidity have been gravimetrically calibrated with samples of stormwater solids and provide an important indication of suspended solid transport rates. As is evident from Figure 3.6 variations of turbidity are characterised by a "first flush" followed by a less important "secondary flush". For 190 storm events, monitored in this way during 1983 and 1984, 54% were characterised by a "first flush" in terms of turbidity (Morrison et al. 1985).

Temperature changes generally follow conductivity and pH, with a decrease in temperature associated with incoming rainfall. However, the slight increase in temperature at the very beginning of the storm event is characteristic of most storm events in autumn. Gullypots are the only reservoir of relatively warm water, compared to baseflow, and

their flushing at the commencement of the storm event seems to be the most likely explanation for this initial temperature increase.

Bergsjön 1st-2nd October 1984

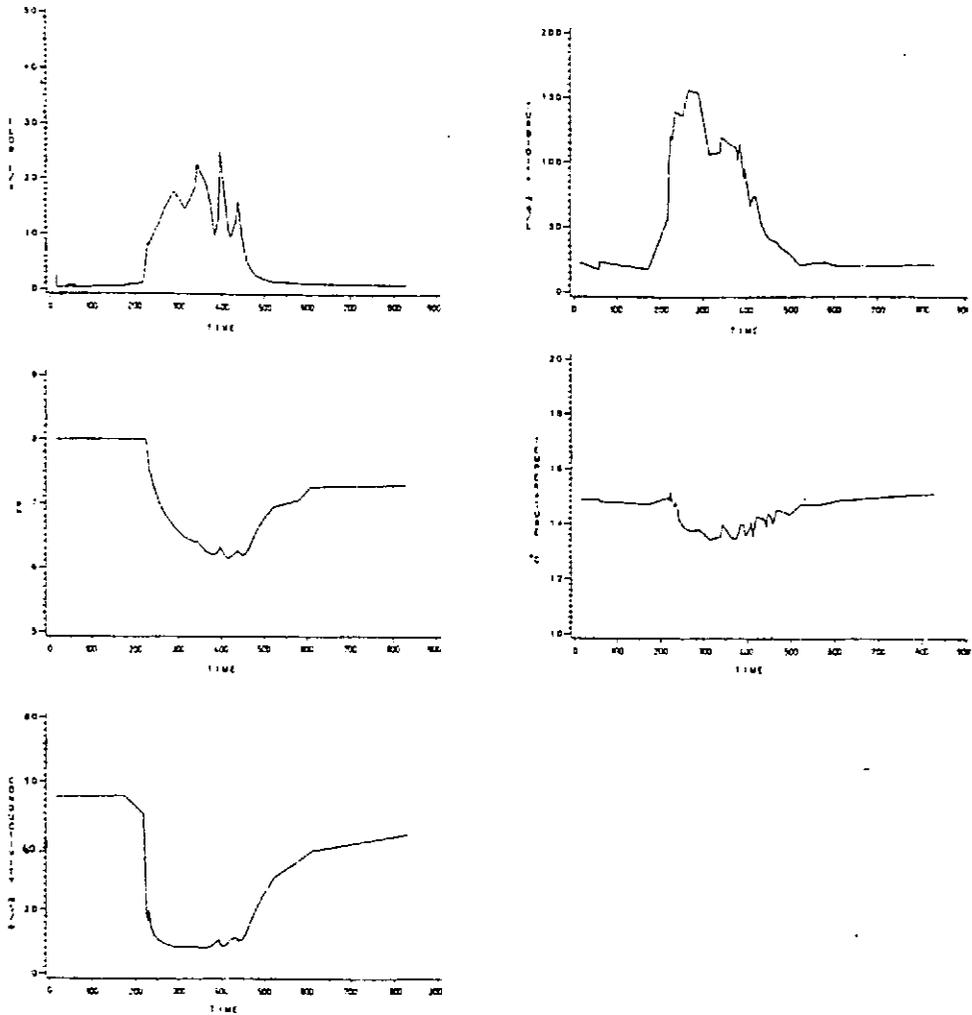


Figure 3.6 Continuous Storm Data for the Bergsjön Field Station. Time in Minutes Commencing 17.00.

### 3.2.5 Sampling.

Water sampling is initiated automatically and is started at a preset water level (usually  $\approx 100$  mm stage height). A switch on the level recorder starts a tipping bucket on the side of the primary sampling tank (Figure 3.7). Twelve sample bottles (one litre) are installed in an adapted refrigerator and the samples are transferred by a stepping motor through polyethylene tubes into the individual bottles. Each bottle collects a sequential composite sample comprising 16-18 samples from the tipping bucket, each tip representing one cubic metre of flow volume.

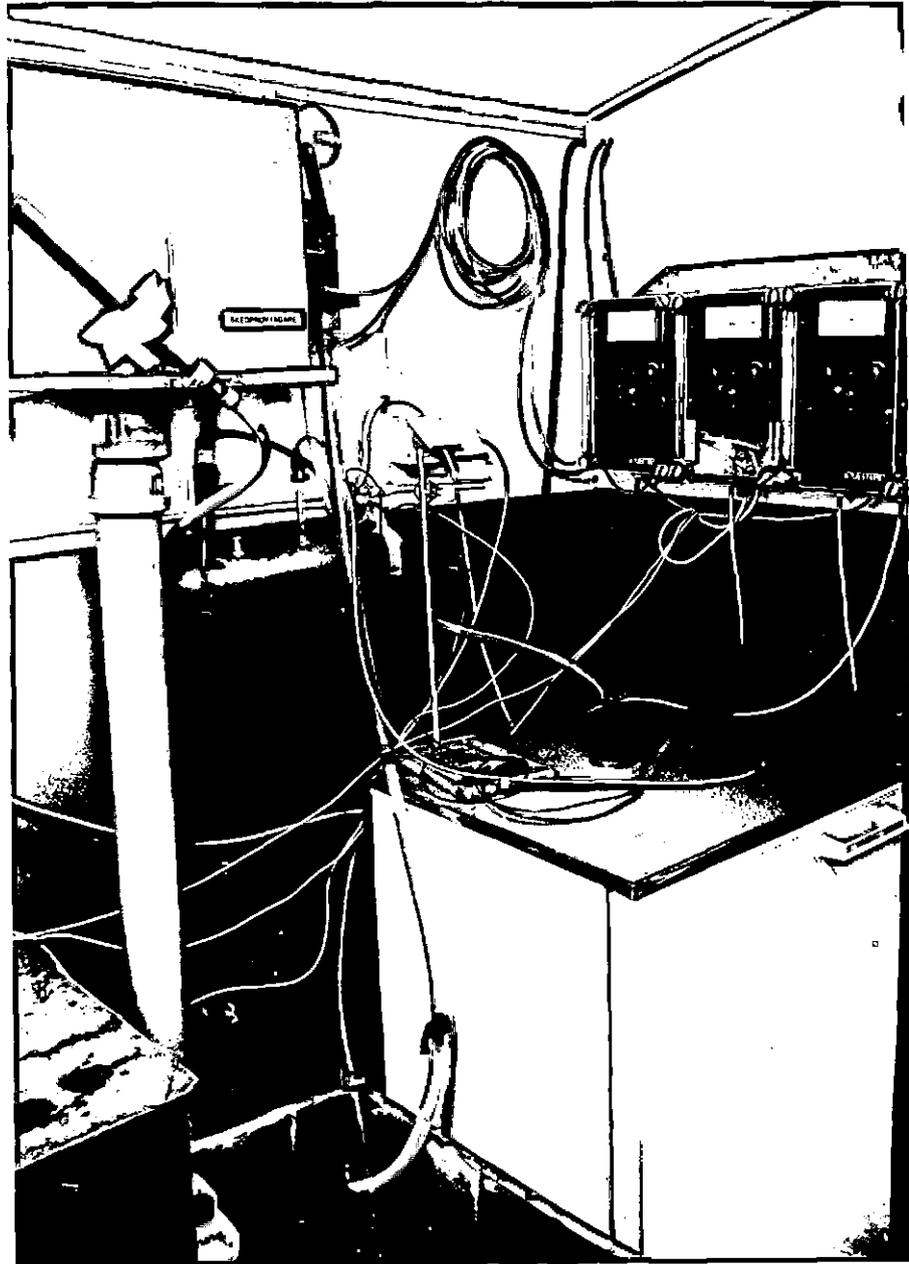


Figure 3.7 Equipment for Sampling and Sample Storage at the Bergsjön Field Station.

### 3.3 The Chalmers Catchment.

The Chalmers catchment comprises an asphalt parking lot which is drained by several gullypots. One of these gullypots, which drains 390 m<sup>2</sup> of the parking lot surface, was chosen for the study (Figure 3.8). Pollutants, including suspended solids and heavy metals, discharging to the gullypot have been investigated previously by Svensson (1983).

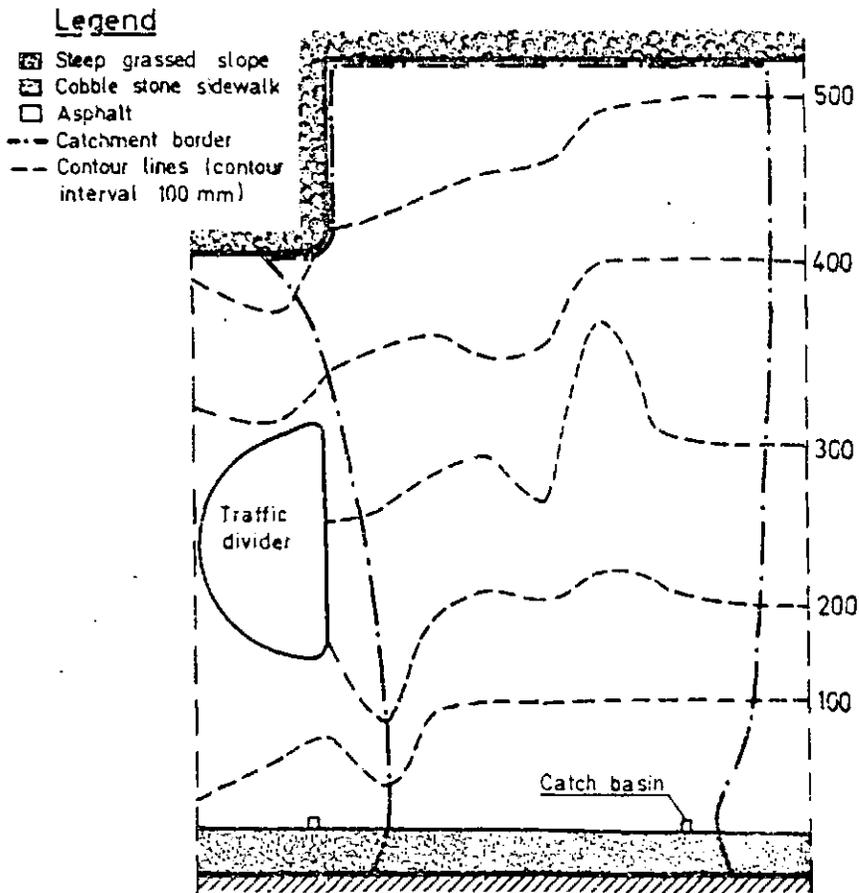


Figure 3.8 Sewered Contributing Areas on the Chalmers Catchment.

### 3.3.1 Catchment Characteristics.

The catchment is almost completely impervious with drainage occurring only from the parking lot, a road and a roadside kerb. Metal contributions may originate from the corrosion of the two lamp posts, from vehicular sources, deposited road dust and road surface material.

#### 3.3.1.1 Depression Storage Value.

The Depression Storage Value for the catchment over a two month study period has been calculated from a plot of rainfall (mm) against total runoff volume (litres). Equation 3.4 describes the linear relationship for 10 events, July/August 1985, with a correlation coefficient of 0.998.

$$y = 0.146 + 0.0016x \qquad 3.4$$

y = Rainfall (mm), x = Runoff (litres).

The Depression Storage Value is the vertical intercept, representing 0.146 mm of rainfall before the commencement of runoff.

### 3.3.2 Flow Measurements.

A gullypot flow measuring device, developed by the University of Lund, Sweden, was used to monitor the depth of road runoff passing through a 30° V-notch weir (Figure 3.9). Flow height is measured by the decrease in resistance between two electrodes which are covered by a saline solution. The conductivity cell is separated from the V-notch flume by a durable moving rubber membrane. The gullypot sampler is positioned in the gullypot chamber so that all the flow is channelled into the flume.

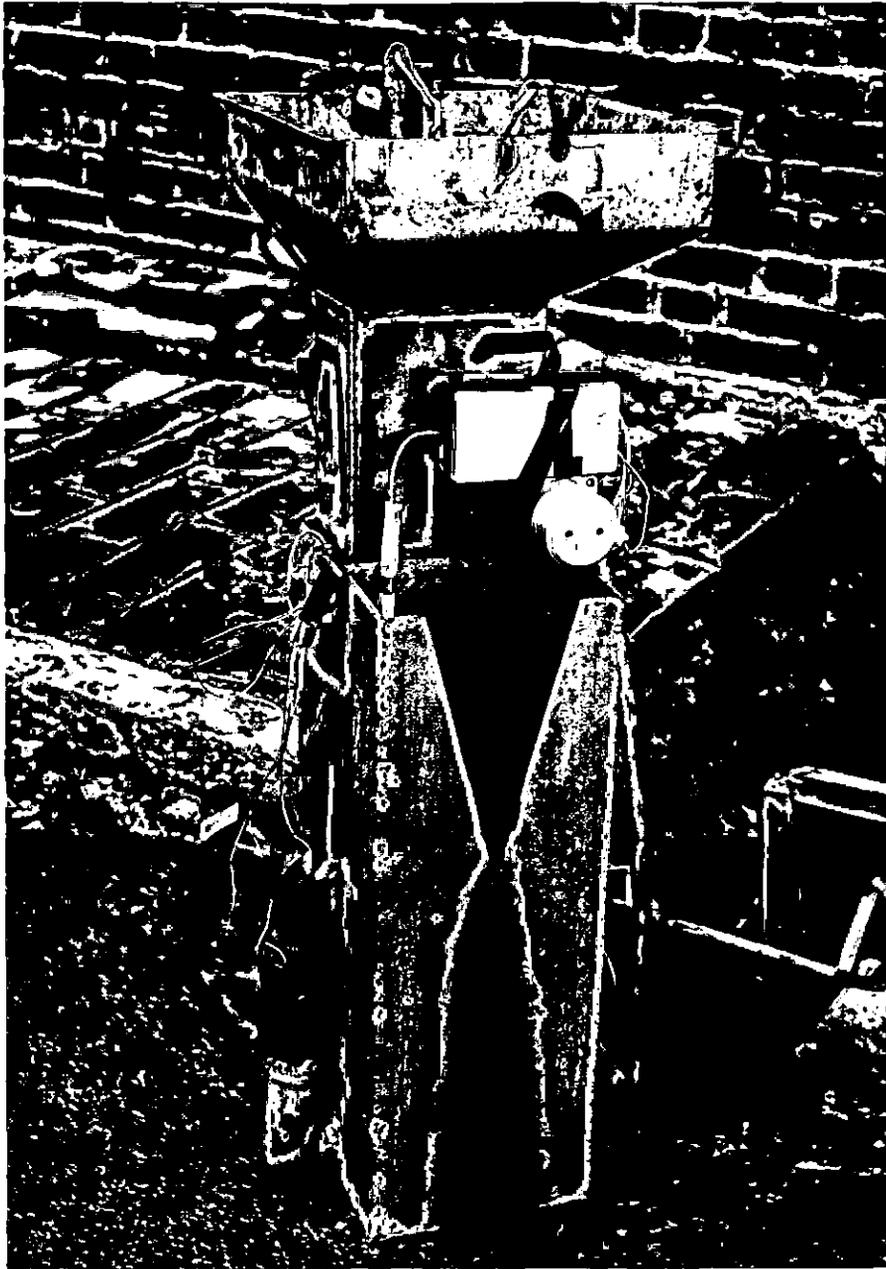


Figure 3.9 Gullypot Road Runoff Sampler showing V-notch Weir for Flow Measurements.

Flow height is recorded on a chart recorder and has been calibrated against flow volume passing through the V-notch. A plot of calibrated flow ( $Q$ ) against chart recorder height ( $h$ ) can be converted to equation 3.5.

$$Q = 0.000145h^{2.495}$$

3.5

Q = Flow (l/s), h = Chart Recorder Height (%), r = 0.99

### 3.3.3 Precipitation Measurements.

A rainfall gauge of the same type as at Bergsjön is situated 100 metres from this catchment.

### 3.3.4 Continuous Pollutant Monitoring at the Chalmers Roadside Gullypot.

The continuous monitoring system, shown diagrammatically in Figure 3.10, is based on that at Bergsjön. The parameters monitored (pH, dissolved oxygen, conductivity and redox) are those which may be important regulators of heavy metal speciation and are included as essential determinands in the monitoring system.

Water is pumped out of the gullypot, through an opening in the basement wall, via a strengthened 12 mm diameter plastic pipe and returned to the gullypot in the same manner after passing through a small Jabasco cog wheel pump and the on-line measurement system. A water flow rate of 2.6 l/min allows a water depth of 30 mm to be maintained in the continuous system which is high enough to prevent blockage by solids. In this way the gullypot contents are recycled every 1.4 hours during dry conditions. Cleaning of the pipes is achieved by reversing the pump and flushing with two to three litres of double distilled water. This procedure is normally repeated twice a week or more frequently during periods of heavy rainfall.

The continuous monitoring system (Figure 3.11) is a sealed PVC pipe, of 50 mm diameter and 400 mm length, with an inlet of 13 mm diameter and an outlet of 25 mm diameter at the opposite end. Calibrated dissolved oxygen, combined redox potential, combined pH and conductivity electrodes are positioned, as shown in Figure 3.10 and Figure 3.11, and the signals are recorded as at Bergsjön.

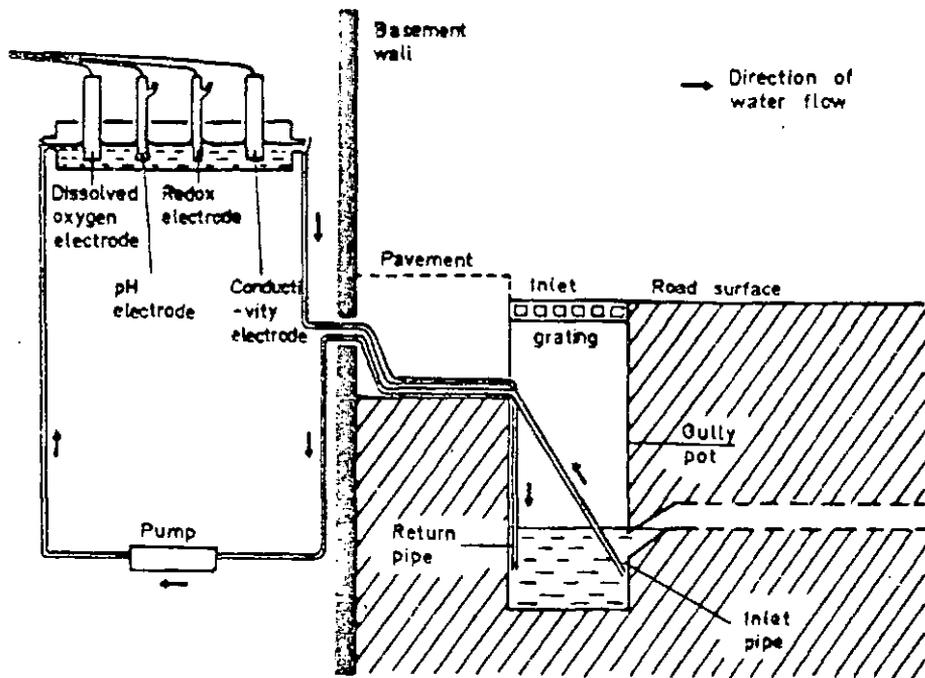


Figure 3.10 The Continuous System for Monitoring the Contents of a Gullypot.

Typical continuous data obtained from the gullypot shows rapid changes and is less complicated than the response at the end of the stormwater pipe network (Figure 3.13). The gullypot has a standing volume of 41.5 litres.

Two distinct types of storm event have been observed in the gullypot, as indicated by the hydrographs and chemographs in Figure 3.12 and Figure 3.13. A small rainfall event of 128 litres runoff is shown in Figure 3.12, which is only sufficient to mix, but not completely flush, the gullypot. A lag period of five minutes is observed between the commencement of flow and any observed change in either dissolved oxygen or redox potential. The significant drop which eventually occurs in redox potential and dissolved oxygen concentration represents mobilisation of the reducing, oxygen demanding interstitial sediment water. At the same time a dissolution of sediment associated salts occurs which, together with mobilisation of liquor and interstitial water, causes a general increase in conductivity at the end of the storm event.

The reading for pH generally increases between storm events from ca. 4.5 up to 7.0, mainly because of dissolution of the gullypot cement structure. However, despite a measured incoming rainfall pH of 4.0 and evidence of interstitial sediment water mobilisation after five minutes, pH changes within the gullypot lag 14 minutes behind the commencement of flow. This represents the residual buffering capacity of the gullypot. The resultant titration curve is a slight overestimate of the gullypot buffering capacity as the road surface and its associated sediments also buffer the acidic rainfall.

A second type of rainfall event is shown in Figure 3.13. This is a heavy summer storm of 4764 litres runoff which appears to have mixed and washed out most of the gullypot contents. In the early stages of the storm the pH, dissolved oxygen and redox potential changes are typical of gullypot liquor and interstitial sediment water mobilisation. The next 30 minutes is characterised by a washing of the gullypot with rainwater that causes a drop in pH and conductivity and an increase of redox potential and dissolved oxygen. During the subsequent heavy rainfall it is expected that reduced gullypot basal sediment is mobilised, causing a drop in redox potential and a corresponding increase of pH. This shows that the residual buffering

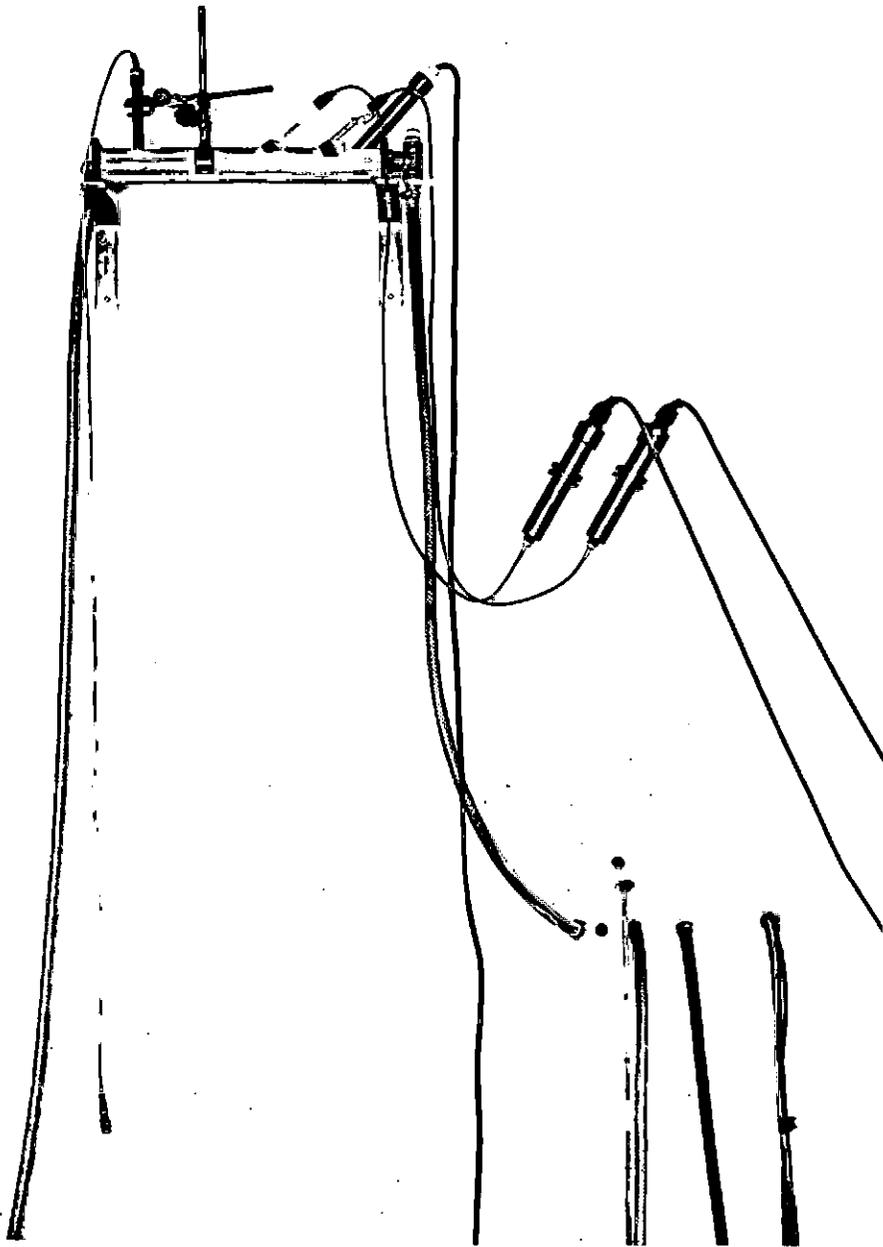


Figure S.11 Continuous Monitoring System inside the Chalmers Basement.

capacity of the gullypot may be increased during intense rainfall due to bottom sediment mobilisation.

CHALWERS GULLYPOT 11 JULY 1984

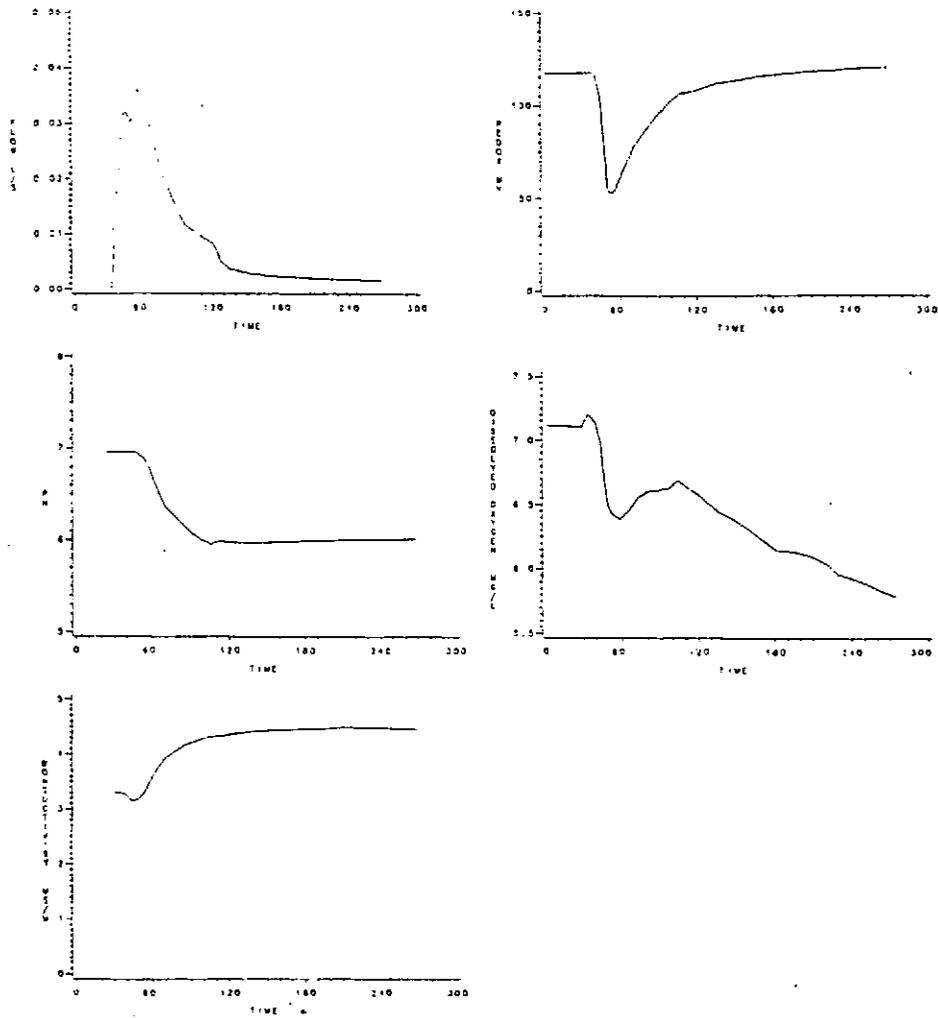


Figure 3.12 Continuous Flow and Pollutant Monitoring for a Small Storm Event in the Gullypot. Time in Minutes Commencing 03.00.

CHALMERS GULLYPOT 28 JULY 1964

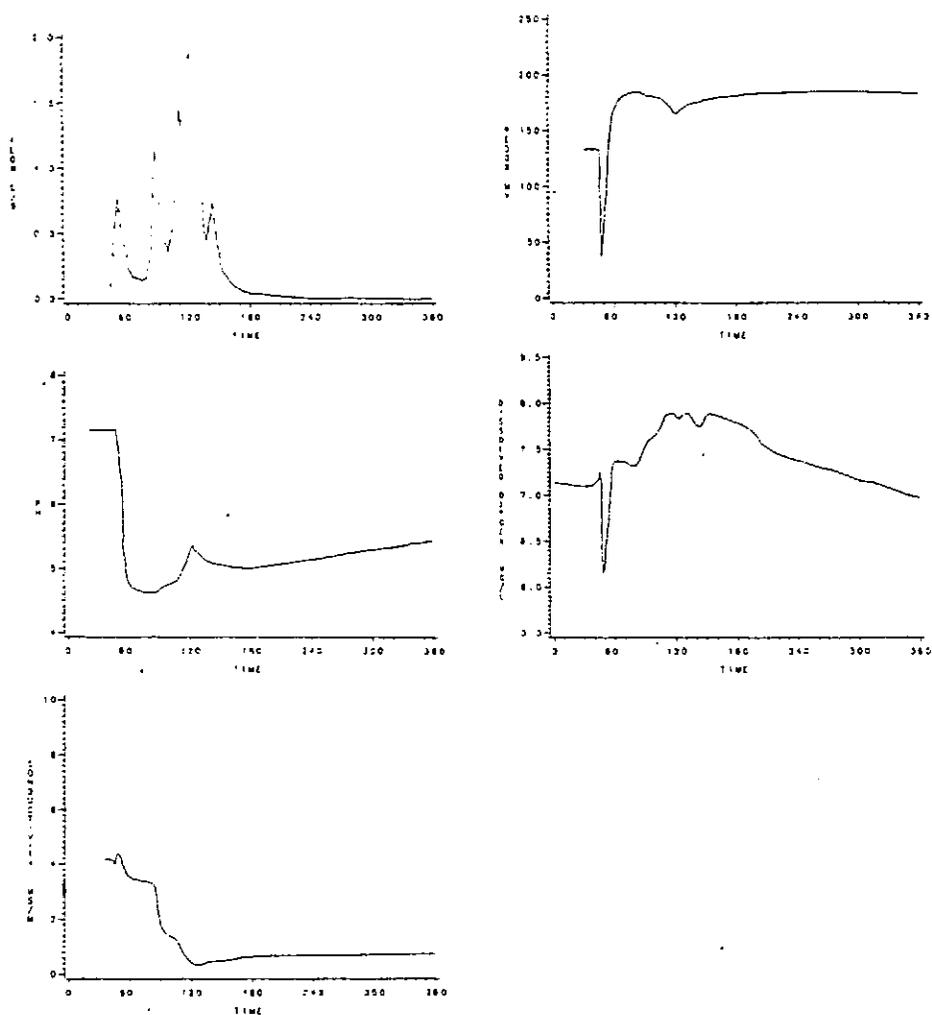


Figure 3.13 Continuous Flow and Pollutant Monitoring for a Heavy Summer Storm Event in the Gullypot. Time in Minutes Commencing 15.00.

Rainwater is saturated with dissolved oxygen and so dissolved oxygen concentrations remained high until the storm event was over. The peak dissolved oxygen concentrations corresponded with high gullypot water inflows. After the rainfall a slow decrease of dissolved oxygen concentration is observed which may be related to bacterial respiration.

3.3.5 Sampling.

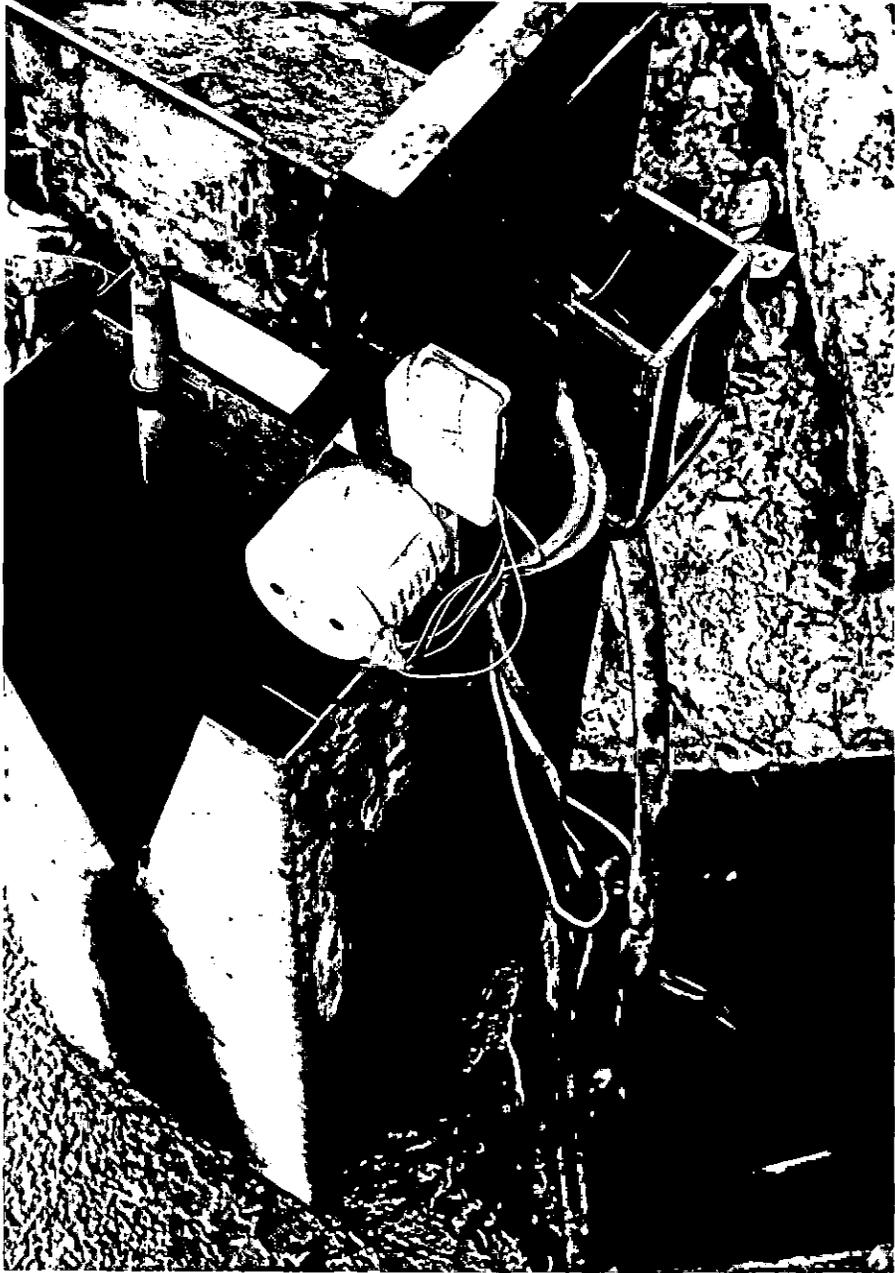


Figure 3.14 Road Runoff Sampler showing Tipping Bucket Sampling Mechanism.

The road runoff entering the gullypot is sampled by the flow measuring device described in 3.3.2. A sensor is located just above the V-notch in the weir (Figure 3.14). When the sensor is reached by the water level a tipping bucket sampler is activated. The samples flow, under gravity, through a rubber hose into the basement of Chalmers University. A step motor sampler (Figure 3.15) receives the water and distributes it into 24 one litre sample bottles. The 40 tipping bucket sub-samples give a one litre sample every three minutes.

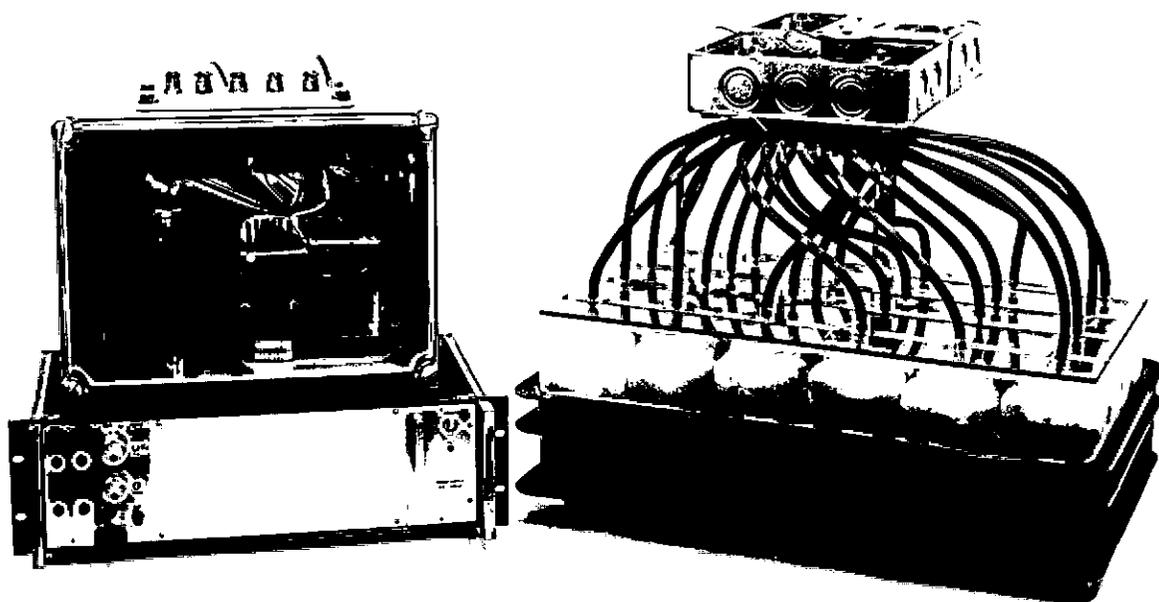


Figure 3.15 Sampling and Flow Measurement Equipment for the Gullypot Experiment.

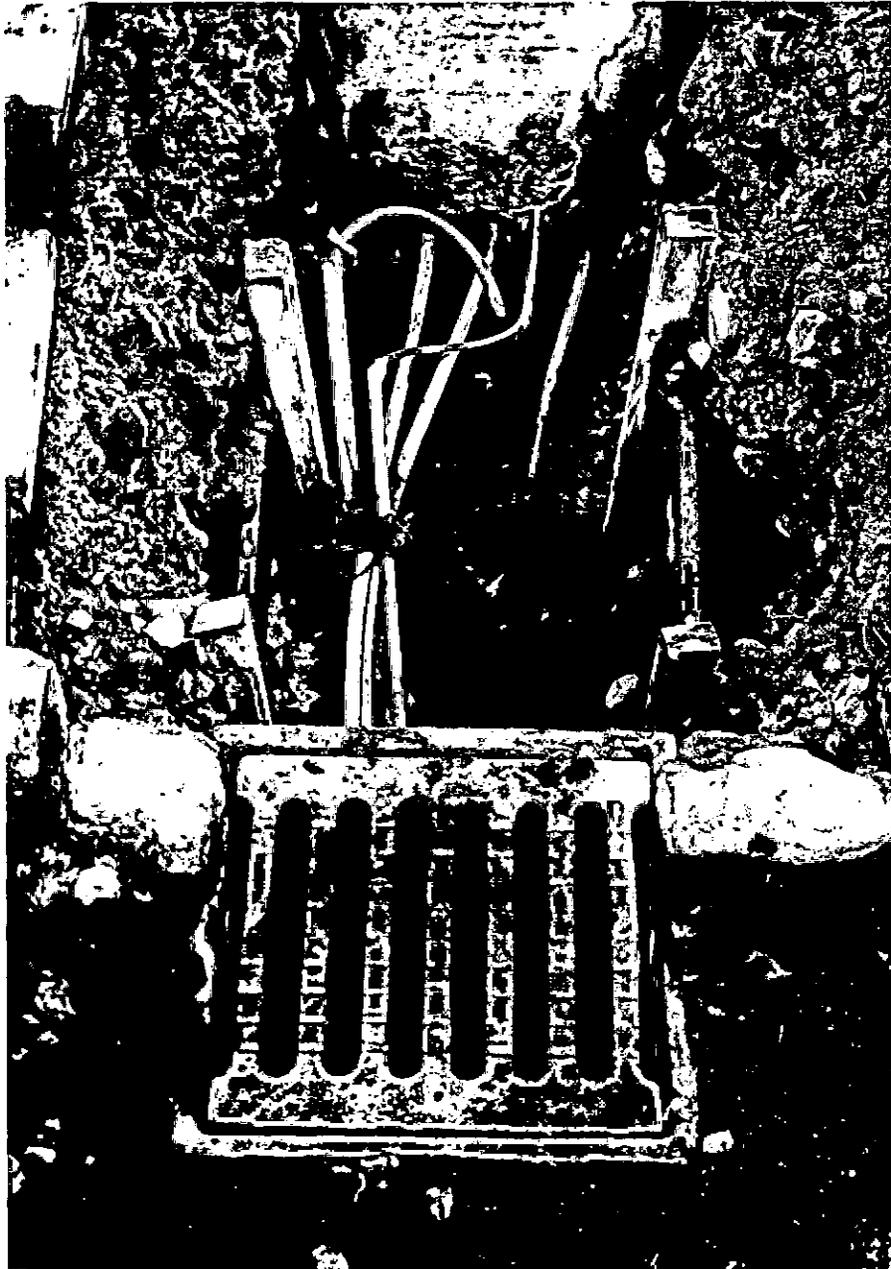


Figure 3.16 Trench from the Gullypot to the Basement of Chalmers University, showing the Outflow Sampling Pipe.

The outflowing water from the gullypot can be sampled manually through a 12 mm polyethylene pipe by gravity feed (Figure 3.16). Bulk precipitation onto the catchment is collected in a polyethylene bottle (1 litre) fitted with a polyethylene funnel and sampled at weekly intervals. Road dusts were collected by means of a wet/dry vacuum cleaner at two week intervals. Two representative sub-areas on the catchment were sampled. The first was an 11.7 m<sup>2</sup> car parking lot and the second a 215 cm long roadside kerb of area 0.65 m<sup>2</sup>. After collection the road dusts were air dried (50°C), weighed and sieved, prior to metal speciation analysis.

## CHAPTER 4 DEVELOPMENT OF THE METAL SPECIATION SCHEME.

The metal speciation scheme was formulated specifically for the fractionation of Cd, Cu, Pb and Zn in stormwater samples. Metal speciation schemes are intended to differentiate the heavy metals into fractions dependent upon their physico-chemical properties. Therefore a satisfactory speciation scheme should allow the identification and evaluation of both toxic and geochemically mobile heavy metals. Most of the schemes which have been developed are applicable to relatively clean, unpolluted, marine and fresh waters and are often too elaborate for routine analysis. In addition, many schemes are only designed for speciating dissolved metals. The high concentrations of suspended solids in stormwater means that for metal speciation purposes the solid phase must also be considered as being of major importance.

In order to interpret toxicity effects, speciation methods need to isolate and quantify the most bioavailable metal. In the dissolved phase this is the free or weakly complexed metal and in the suspended solid phase it is the readily exchangeable metal. Separation of the metal species into fractions cannot therefore be regarded as an exact chemical separation, but simply enables an understanding to be reached concerning relative metal availabilities.

### 4.1 Speciation Scheme for Stormwater Analysis.

A speciation scheme has been developed, following an assessment of the previously described literature concerning this subject (Chapter 2), and by performing a number of relevant background experiments. One requirement was for a well balanced scheme which was experimentally easy to perform and was not extensively time consuming. A further objective was the provision of a complete analysis (including both dissolved and particulate associated metals) which would provide relevant information on bioavailable and total heavy metal levels. The speciation scheme which has been devised to fulfil these criteria is shown in Figure 4.1.

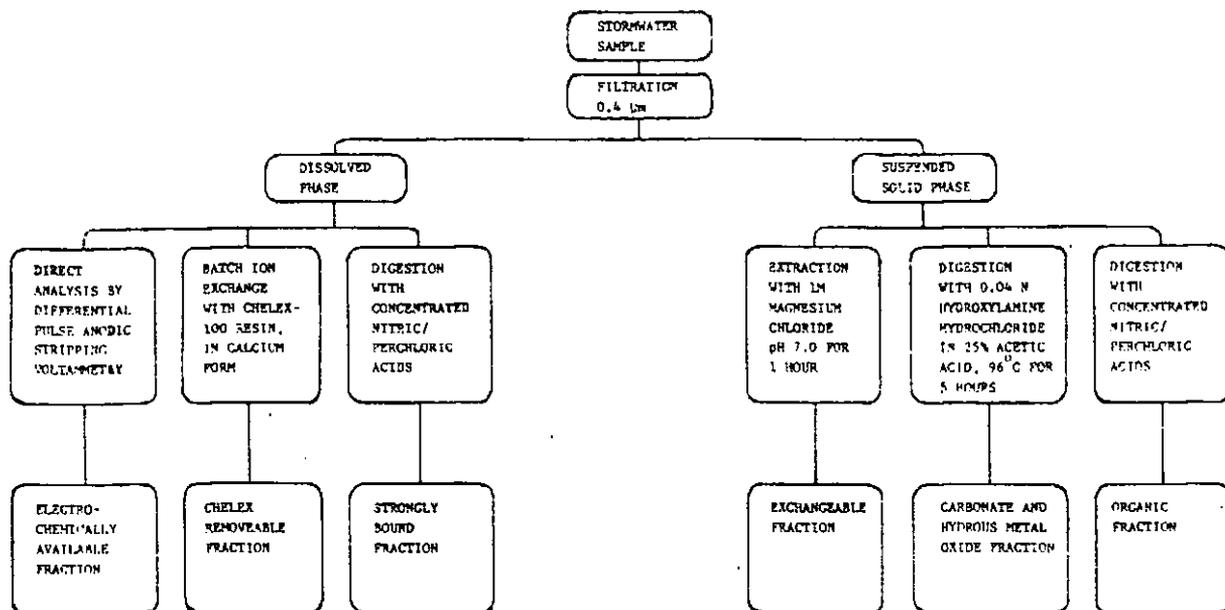


Figure 4.1 Speciation Scheme for Analysis of Heavy Metals in Stormwater.

A preliminary separation allows an operationally defined distinction between the dissolved and suspended solid phases. This was achieved by filtration, normally of 250 ml of sample, through two separate 0.4 µm Nucleopore polycarbonate filters. The heavy metals in the soluble and insoluble phases were then chemically extracted into different fractions depending on their relative ease of release. The suspended solid phase was air dried at 50°C to constant weight and stored in a dessicator. The dissolved phase was stored at 4°C prior to analysis.

The dissolved phase was separated into three fractions depending on the complexation strength of the heavy metals.

a) Electrochemically Available Fraction.

An aliquot (10 ml) of the dissolved phase was analysed for heavy metals by ASV. 2M sodium acetate (0.1 ml) at the pH of the natural

sample was added before analysis. This acts both as a buffer and a support electrolyte. The analytical conditions employed were as follows;

Plating time = 180 seconds

Equilibration time = 30 seconds

Deoxygenation period = 240 seconds

Initial Potential = -1.3V (Zn), -0.9V (Cd, Pb) or -0.3V (Cu)

Scan Rate = 2 mV/s

The plating (electrochemical deposition) time is a compromise between the higher precision of shorter plating times and the higher current response of longer plating times. Equilibration time, deoxygenation period and scan rate are optimised for the Princeton Applied Research Polarographs (Model 174 and 384A) used in this study. The Initial Potential was set individually for Zn (-1.3V) and Cu (-0.3V) and simultaneously for Cd and Pb (-0.9V). The measurement of all four metals in one stripping process produces higher concentrations of Cd, Pb and Cu due to the reduction of strongly bound metal species (Figura and McDuffie 1980) and was therefore avoided.

The Electrochemically Available fraction determines free ions and weakly complexed metals and can be compared to the bioavailable metal as defined by Whitfield and Turner (1979).

#### b) Chelex Removeable Fraction.

An aliquot (50 ml) of the dissolved phase was added to prepared Ca Chelex-100 (500 mg) and equilibrated by shaking continuously for 24 hours. The heavy metals were then eluted off the Chelex resin with 1M HNO<sub>3</sub> (10 ml) which was finally washed with water (10 ml). Water was double distilled and further purified in a Milli-Q deionisation system. After making the eluant up to a total volume of 25 ml, the metal levels in an aliquot (7 ml) were determined by ASV following the addition of 2M sodium acetate (3 ml). The amount of sodium acetate used was sufficient to adjust the sample pH to approximately 4-4.5, which is the most sensitive range for the ASV determination of metals. The ASV conditions were the same as those used for the

Electrochemically Available fraction except that Zn, Cd and Pb were determined simultaneously (Initial Potential = -1.2V) and Cu separately (-0.4V). This was deemed necessary by the possibility of intermetallic interferences which are discussed in 4.3.1.1.

Chelex-100 is a metal selective ion-exchange resin, which removes those metals associated with the Electrochemically Available fraction as well as more strongly bound metals. However, this resin does not retain metals which are strongly bound to colloids or complexes (Figura and McDuffie 1979). Florence et al. (1983) have shown that this fraction may over-estimate the truly bioavailable metal but it does give an indication of those metals attached to ligands by a medium complexation strength.

#### c) Strongly Bound Fraction.

The Strongly Bound metals were released by acid oxidation and calculated as the difference between the metal levels obtained by total acid digestion and by the use of Chelex-100. Concentrated nitric acid (0.18 ml) and concentrated perchloric acid (0.02 ml) were added directly to an aliquot (25 ml) of the dissolved phase. After evaporation to dryness in a fume cupboard the metal perchlorates were taken up in 1M HNO<sub>3</sub> (10 ml) and determined in the same way as the Chelex Removeable fraction.

The experimental conditions used to determine this fraction indicate the strong association of the metals as complexes or colloids and ensure that they may be considered non-bioavailable as far as receiving water biota are concerned.

The suspended solid phase was separated into three fractions according to the ease of release of the metals. The first two digestions were carried out in stoppered polyethylene tubes, in a water bath, at controlled temperatures. The final digestion was carried out in a pyrex beaker (50 ml).

**d) Exchangeable Fraction.**

1M MgCl<sub>2</sub> at pH 7.0 (10 ml) was added to the dried suspended solid phase and agitated at room temperature for one hour. The supernatant liquid was separated by centrifugation at 5000 rpm for 30 minutes and again after washing with water (10 ml). The two supernatants were combined and an aliquot (9 ml) determined by ASV, after the addition of 2M sodium acetate (1 ml).

Particulate associated heavy metals which exchange or complex with anions may be released into the soluble phase of stormwater under normal pH conditions. This solubilisation process is particularly probable under the conditions of high chloride concentrations which are often encountered in urban stormwater and during snowmelt runoff.

**e) Carbonate and Hydrrous Metal Oxide Fraction.**

The suspended solids from (d) above were digested with 0.04M NH<sub>2</sub>OH.HCl in 25% glacial acetic acid (10 ml) at 96°C for five hours. The solids were washed with water (10 ml) after centrifugation. An aliquot (7 ml) of the combined supernatants was analysed by ASV following the addition of 2M sodium acetate (3 ml).

The metals in this fraction are more strongly bound than the Exchangeable fraction and occur mainly as surface associated metals (Davis and Leckie 1978) and co-precipitates of hydrrous metal oxides and carbonates. This fraction is unlikely to have any immediate biological impact on the receiving waters, but may accumulate in river or estuarine sediments. Subsequently the metals may be released into the water column when a significant drop in pH occurs (Florence and Batley 1980).

#### f) Organic Fraction.

These strongly bound metals were released by digestion with nitric and perchloric acids (9:1). Concentrated nitric acid (18 ml) and concentrated perchloric acid (2 ml) were added directly to the suspended solid phase from (e). The mixture was covered with a watch glass and boiled for two hours, until the nucleopore filters and sediment were digested and, after removing the watch glass, taken to dryness. The residue was taken up in warm 1M HNO<sub>3</sub> (10 ml) and water (10 ml). Heavy metals in the combined extract were determined in the same way as the previous fraction.

These remaining metals are largely organically bound in polluted solids or sediments and because of their strong association are unlikely to be bioavailable. However, this fraction may act as an important transportation mechanism and sink for such metals as Pb and Cu, which have high stability constants with organic compounds (Mantoura et al. 1978).

The scheme required some preliminary investigation before it could be applied to stormwater. To interpret the results obtained it is necessary to understand which metal species are likely to be in each fraction, and to examine interferences to the analysis.

#### 4.2 Separation of the Dissolved and Suspended Solid Phases.

The separation of dissolved and suspended solid associated metals is operationally defined by filtration through a 0.45 or 0.4  $\mu$ m filter (Stumm 1983). Colloidal species are found in both the dissolved and suspended solid phases but can be separated by a series of different sized filters (Laxen and Harrison 1981a). However, separation of metal fractions on the basis of size alone provides little, if any, information about the relative potential toxicity of the species present. Centrifugation was not chosen as the preliminary step due to the changes in metal speciation which might be caused by carrying down dissolved metals on colloids (Buffle 1984).

Nucleopore 0.4  $\mu\text{m}$  polycarbonate filters provide a barrier for metal species larger than 0.4  $\mu\text{m}$ . However, filtration of stormwater samples of volume greater than 100 ml is not possible with a single filter due to the presence of colloids, which cause blockage and may also result in a change in the diameter of the filter pores. A pre-filtration with a 5  $\mu\text{m}$  filter was not found to give any significant filtration rate improvement. However, a satisfactory overall filtration was achieved by using two Nucleopore filters separately for a 250 ml stormwater sample, which typically contains 50-200 mg/l suspended solids.

Millipore 0.45  $\mu\text{m}$  filters are membrane depth filters which, although they have a less precise cut-off value compared to Nucleopore filters, can effectively filter up to 250 ml stormwater containing typical suspended solid levels. These filters were used when high suspended solid concentrations rendered Nucleopore filtration impossible. This was necessary for the majority of the gullypot samples.

Nucleopore and Millipore filters are not guaranteed to be in a metal free form when received from the manufacturers. They were therefore placed in a 10%  $\text{HNO}_3$  bath overnight and washed thoroughly with water, before use. The acid wash resulted in negligible metal blank values for both types of filter.

#### 4.3 Analysis of the Dissolved Phase.

Dissolved metals can be separated into fractions depending on their complexation strength or lability. There are several methods (previously outlined in Chapter 2) for chemically characterising different fractions including;

- a) Direct voltammetric analysis
- b) Resin extraction
- c) Ultra-violet irradiation
- d) Oxidation by concentrated acids
- e) Dialysis

Direct voltammetric analysis was chosen in this study because of its ability to directly identify free metal ion and weakly complexed metal species, which are likely to be the forms available to receiving water biota. The metal concentration difference between acid oxidation and Chelex-100 extraction was the method selected to separate the Strongly Bound fraction. These metal forms may be regarded as being inert to the biological membrane.

#### 4.3.1 Initial Analytical Problems for the Dissolved Phase.

A number of procedural problems with the analysis of dissolved metal species were originally encountered. These have been investigated as described below and the necessary modifications instituted to give an overall method suitable for stormwater analysis.

##### 4.3.1.1 Organic and Inorganic Interferences in Direct Voltammetric Analysis.

a) It was not possible to analyse all four metals simultaneously by ASV due to the formation of intermetallic compounds. At metal concentrations of 100 µg/l a significant increase of Cu peak height was observed in the presence of Zn. This effect was tested by varying the Initial Potential to include or exclude the latter metal. Copper and Zn were subsequently determined at separate Initial Potentials of -0.4 or -0.3V and -1.3V or -1.2V respectively. No other intermetallic interactions were observed.

b) It was observed that the ASV peak height for metals in stormwater samples became greater with the use of increasingly negative potentials, which is in agreement with the results of Figura and McDuffie (1979). This was thought to be due to the increased liberation of metals from stronger complexes by more negative potentials. The ASV labile metals were therefore determined using the following Initial Potentials: Zn -1.3V, Cd and Pb -0.9V, Cu -0.3V. Figure 4.2 shows that all four metals can be determined in a stormwater sample by this method. The shift in potential which can be encountered due to organic surfactants (Beveridge and Pickering 1984)

was not observed. However, standard additions were always used for calibrating the Electrochemically Available fraction.

ELECTROCHEMICALLY AVAILABLE METAL  
STORMWATER SAMPLE, BERGSJÖN, pH 5.3

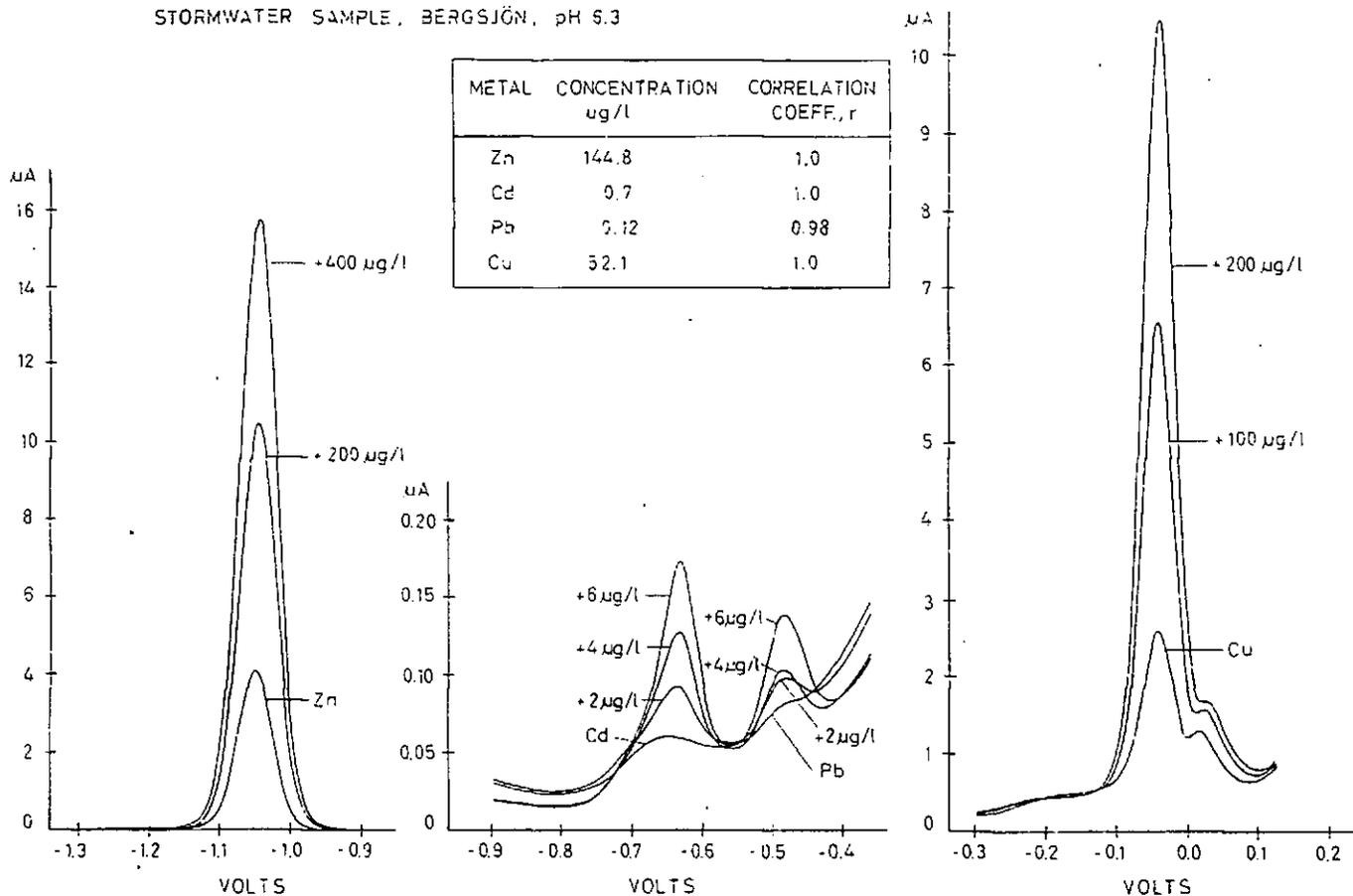


Figure 4.2 ASV Determination of Metals in a Stormwater Sample.

c) It was found that the most reproducible ASV measurements of the Electrochemically Available fraction were obtained with the sample held in a polyethylene cup, and with the addition of buffer at the sample pH. This is shown for a stormwater sample, containing 52.1  $\mu\text{g/l}$  of Electrochemically Available Cu, in Figure 4.3.

ELECTROCHEMICALLY AVAILABLE COPPER,  
STORMWATER SAMPLE, BERGSJÖN

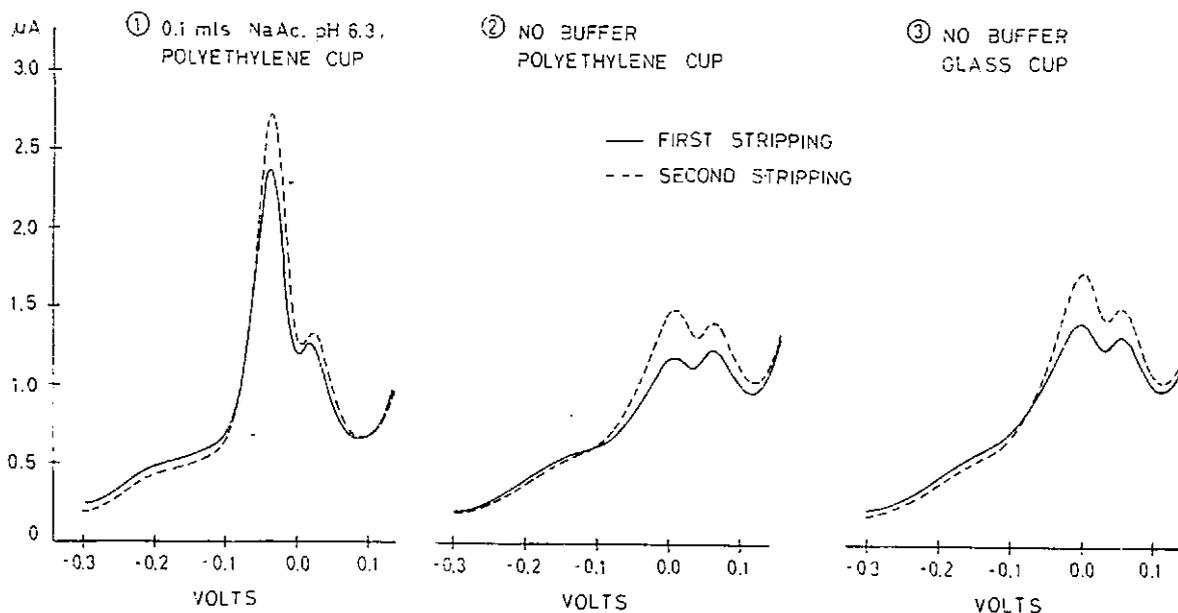


Figure 4.3 Electrochemically Available Copper Response under different Analytical Conditions.

The addition of buffer provides a more distinct peak response at the free Cu potential (-0.03V). Without the addition of buffer to the sample a second stripping in the same solution provides a significantly higher peak which could be attributed to pH changes during deoxygenation or partial lability of metal complexes (Sterritt and Lester 1984). Although there was no significant difference for the peak height obtained in a glass cup over that in a polyethylene cup, adsorption of ionic metal to glass can easily occur (Florence 1982) and therefore a polyethylene cup was preferred.

d) High levels of chloride, as found in snowmelt runoff, produced a significant negative shift of potential for Pb (-0.05V) and Cu (-0.06V). This can be seen by a comparison of Figures 4.2 and 4.4 and is presumably due to the formation of chloride complexes.

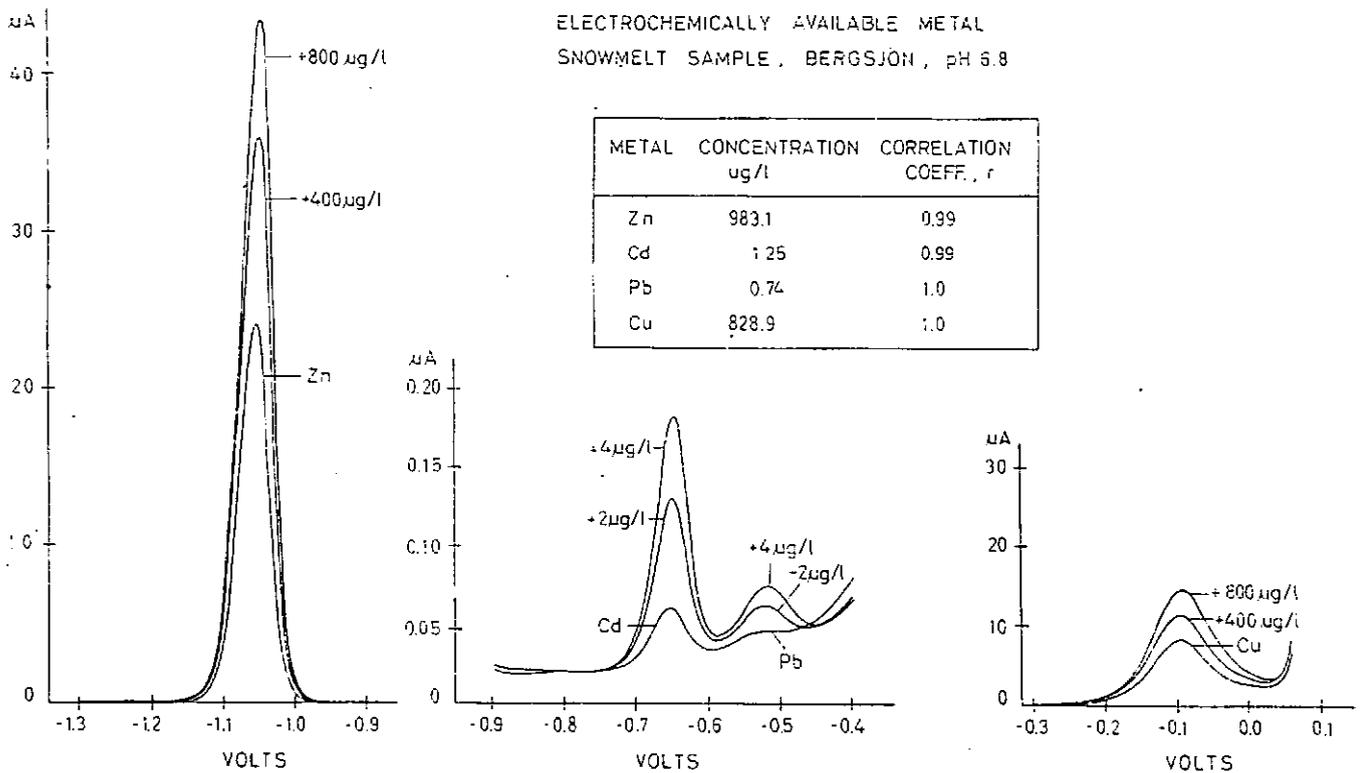


Figure 4.4 ASV Determination of Metals in a Snowmelt Sample.

#### 4.3.1.2 Column and Batch Extraction with Chelex-100.

Figura and McDuffie (1978) found that the Ca form of Chelex-100 provided the least change to the sample pH. Subsequently in this work it was noted that the effluent of the Ca Chelex batch extraction had a pH of 7.5-7.6, which is therefore the pH for metal uptake onto the resin.

The use of Chelex in a batch technique was preferred to the column method as the latter separates metals on the basis of contact timescale and, apart from the column being difficult to standardise, the ASV measurement already provides a similar measurement. The batch method reaches equilibrium after one hour (Hart and Davies 1977), although the equilibration was allowed to proceed for 24 hours to make

certain of completion. Batch fractionation represents those species with stability constants less than the Chelex-100 chelating functional group, as well as colloidal bound species which can enter the macroporous structure of the resin.

During preliminary work it was not certain whether 1M HNO<sub>3</sub> (10 ml) would elute all the metals attached to the Chelex. Analysis showed that neither further elution with 1M HNO<sub>3</sub> nor elution with 2M HNO<sub>3</sub> provided additional metal release from the column.

#### 4.3.1.3 Oxidation by Strong Acids.

Acid oxidation was considered the most suitable method for liberating all the dissolved metal, regardless of their complexation strengths.

Calculations have shown that 0.18 ml of concentrated HNO<sub>3</sub> and 0.02 ml of concentrated HClO<sub>4</sub> should be sufficient to completely destroy all the organics contained in a 25 ml stormwater sample. The acidified sample was always heated to dryness, to remove residual acid, before taking up the metals in 1M HNO<sub>3</sub>. In this way the possibility of interferences by residual perchloric acid traces during the ASV measurement was eliminated. The presence of residual concentrated acid also caused a hydrogen over-potential at -1.2V to -1.1V, which obscured the Zn peak.

For both the Chelex batch method and the acid oxidation the metal was taken up in 1M HNO<sub>3</sub> (10 ml) and made up to volume (25 ml) with water. When a metal analysis was performed by ASV it was found necessary to add 2M sodium acetate (3 ml) to the acidic analyte (7 ml) to give a sufficiently high pH to prevent the hydrogen over-potential interfering with the Zn analysis.

#### 4.3.2 Application of the Proposed Scheme to a Preliminary Sample.

A preliminary analysis was performed on an urban stream baseflow sample collected from the Colindeep Lane sampling station which is

located at the outfall to the Grahame Park catchment, N.W. London. The sample was filtered through a 0.4  $\mu\text{m}$  Nucleopore filter and the dissolved phase analysed for the Electrochemically Available, Chelex Removeable and Strongly Bound fractions according to the scheme described in 4.1. The sample (pH 6.9) contained 48 mg/l suspended solids.

The metal concentrations in the different fractions are listed in Table 4.1 and are illustrated graphically in Figure 4.5.

Table 4.1 Metal Speciation for a Preliminary Sample.

Fraction	Zinc $\mu\text{g/l}$	Cadmium $\mu\text{g/l}$	Lead $\mu\text{g/l}$	Copper $\mu\text{g/l}$
Electrochemically Available	115.5	0.4	nd	nd
Chelex Removeable	150.0	0.5	7.25	18.0
Total Metal	159.0	2.0	10.4	22.5

n.d. = not detected

The scheme shows a clear fractionation of metal species with a greater amount in the Chelex Removeable fraction compared to the Electrochemically Available fraction. This is expected as Chelex-100 should remove all metal species, except those that are strongly bound, while the Electrochemically Available fraction only detects free metal and certain weakly complexed metal species. Zinc and Cd are clearly present in relatively free forms, while Cu and Pb are to a

great extent complexed with no metal in the Electrochemically Available fraction.

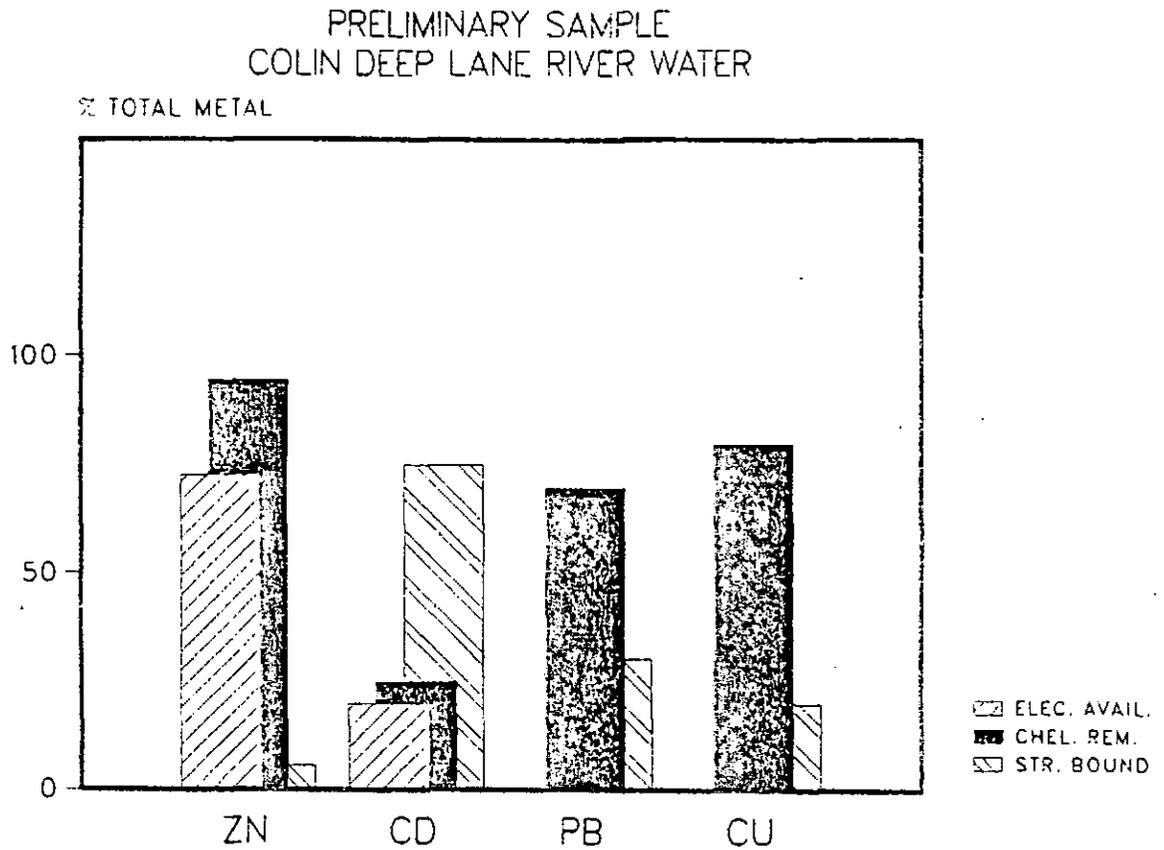


Figure 4.5 Metal Fractionation in a Preliminary Sample.

#### 4.4 Analysis of the Suspended Solid Phase.

Although the toxicity of the dissolved phase is higher, because of its direct contact with organisms, the non-lithogenic fractions of suspended solids may subsequently release heavy metals into aqueous systems. The fractions studied must therefore reflect all heavy metal species which might have an effect on the aquatic biota, or become geochemical sinks.

The suspended solid phase may be divided into fractions according to the ease of metal release. These fractions include:

- a) Exchangeable fraction
- b) Carbonate fraction
- c) Hydrous metal oxide fraction
- d) Organic fraction
- e) Residual fraction

The Exchangeable fraction was selected for measurement in this study as it represents metals which may be released from stormwater solids under normal pH conditions and when changes in ionic strength occur. The latter situation is particularly relevant to snowmelt runoff where high chloride concentrations occur.

The Carbonate and Hydrous Metal Oxide fractions were analysed together to represent those metals which are released when the water is acidified and/or where reducing conditions are encountered, such as in a gullypot.

The Organic fraction contains strongly bound metals and so it can act as a sink. Where sediments are remobilised the fraction can help to transport metals. Such a case could be the resuspension of storm deposited river sediments by heavy urban runoff discharges.

#### 4.4.1 Initial Analytical Problems for the Suspended Solid Phase.

Analytical problems encountered with the extraction and analysis of metals in the suspended solid fractions are described below.

##### 4.4.1.1 Weight Loss of Filters.

The Nucleopore and particularly the Millipore filters were found to lose weight when dried at 50°C. Therefore, before weighing, the filters were dried overnight at 50°C and stored in a dessicator.

#### 4.4.1.2 Effect of H<sub>2</sub>O<sub>2</sub> on ASV Measurements.

Although not subsequently used as an extraction technique, the analysis of the organic fraction after digestion with H<sub>2</sub>O<sub>2</sub> (Tessier et al. 1979) was difficult by ASV. It was found that direct ASV analysis of this extract gave a broad peak between -1.0V and -1.2V which prevented the analysis of Zn. To avoid this interference it would be possible to reduce the extract to dryness and redissolve the metals in 1M HNO<sub>3</sub> followed by direct ASV analysis. It was also observed that the direct analysis of the H<sub>2</sub>O<sub>2</sub> extract caused changes to the Hg drop during ASV with the formation of smaller drops and a subsequent effect on the Hg in the capillary, which created problems in later analysis. The use of H<sub>2</sub>O<sub>2</sub> extraction prior to ASV analysis is therefore to be avoided.

#### 4.4.1.3 Digestion of the Filter.

During extraction of the Organic fraction it was found preferable to completely digest the filter using strong acid before evaporating to dryness. This is necessary due to the fact that when some of the filter was not digested a dark residue was obtained. When taken up in 1M HNO<sub>3</sub> and analysed by ASV the extract gave a broad peak around -0.5V which completely obscured the Pb peak. Nucleopore filters created the greatest problem and so when digesting with concentrated acids a watch glass was placed over the hot mixture for about one hour to allow complete digestion of the filter.

#### 4.4.2 Efficiency of the Chosen Extraction Scheme.

The appraisal of the literature (see 2.6.1) revealed that the different sediment fractions are not strictly selective for individual metal species. It was felt that some improvements could be made, particularly in the case of the Organic fraction. In addition the choice of a one molar concentration of MgCl<sub>2</sub> for the Exchangeable fraction (Tessier et al. 1979) seems to be somewhat arbitrary.

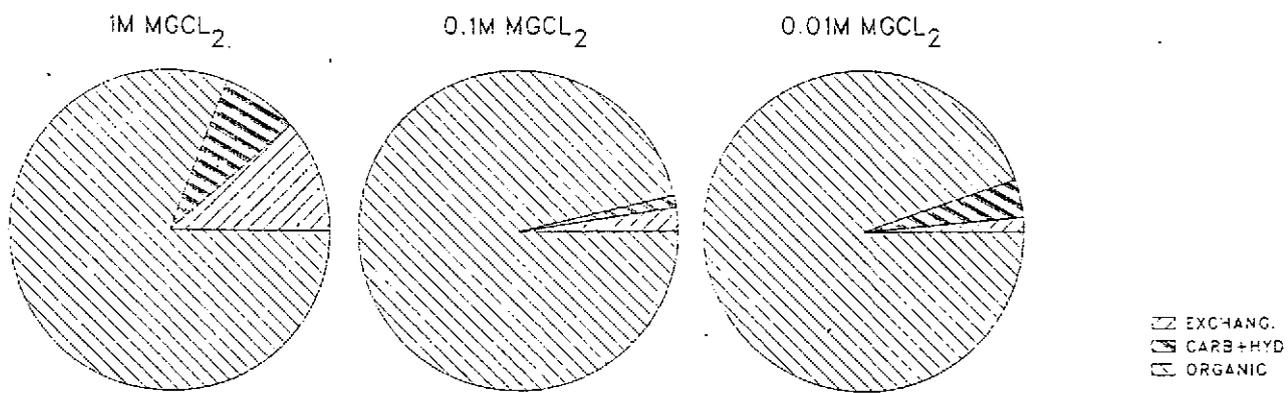
#### 4.4.2.1 Effect of different MgCl<sub>2</sub> Concentrations on the Metal Extraction Efficiency.

A commonly used extractant for determining those metals which are readily exchangeable is 1M MgCl<sub>2</sub> at pH 7.0. To assess the applicability of 1M MgCl<sub>2</sub> for this fraction it was decided to compare the extraction efficiencies of different MgCl<sub>2</sub> concentrations. This would give not only an idea of how different degrees of road salting might release each metal from the solid to the liquid phase, but also indicate whether a concentration as high as 1M MgCl<sub>2</sub> is required for efficient extraction.

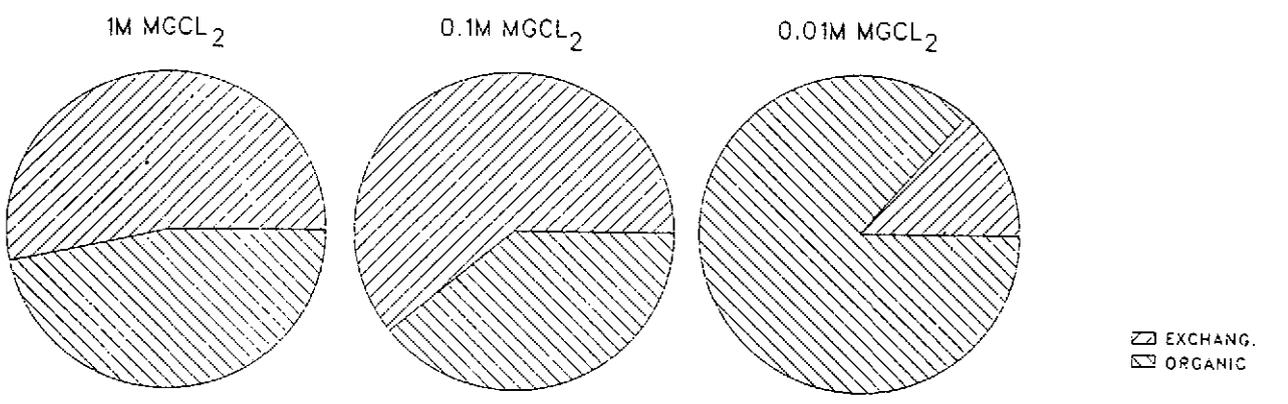
A bulked sample from a storm at Bergsjön was filtered and three sub-samples (0.1g) were extracted in duplicate with 1M, 0.1M and 0.01M MgCl<sub>2</sub> at pH 7.0. All samples were subsequently analysed for Carbonate and Hydrated Metal Oxide, and Organic associated metals.

The results are expressed in a pie chart form (Figure 4.6) to allow easier interpretation of the data. The metal percentages extracted show that for Zn, Pb and Cu, 1M MgCl<sub>2</sub> is required to remove significant metal concentrations. Cadmium, however, is efficiently extracted with 0.1M MgCl<sub>2</sub> which is related to the formation of strong chloro complexes for this metal. The removal of Cu, Pb and Zn may be due to the exchange with Mg<sup>2+</sup> at particulate organic sites as the high concentration of Mg<sup>2+</sup> offsets its lower stability constant with organic carbon compared to the heavy metals.

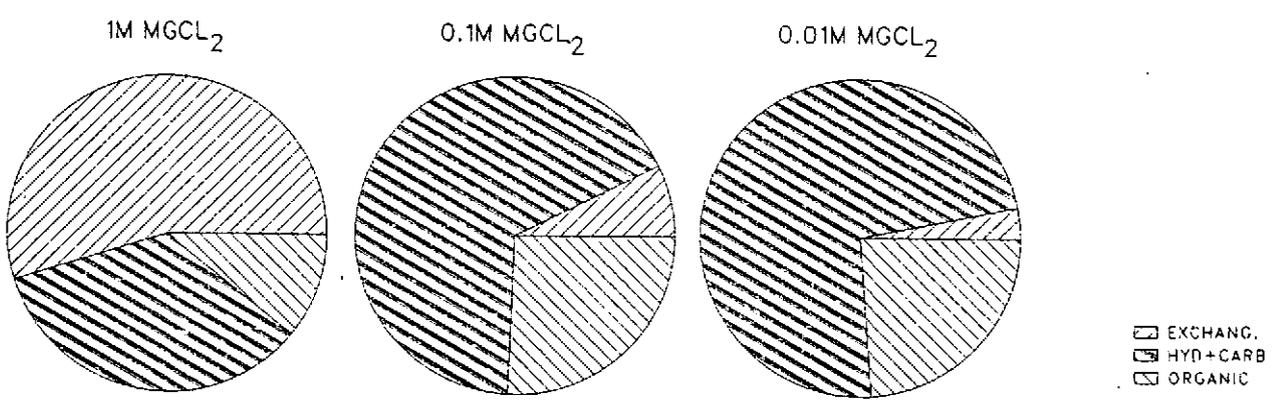
Washing and rewashing of urban sediments with snowmelt runoff, which often has a high ionic strength, would be expected to readily release Cd. During periods of increasing ionic strength in the snowmelt a relative order of release would be; Cd, Cu / Pb, Zn.



CADMIUM



LEAD



COPPER

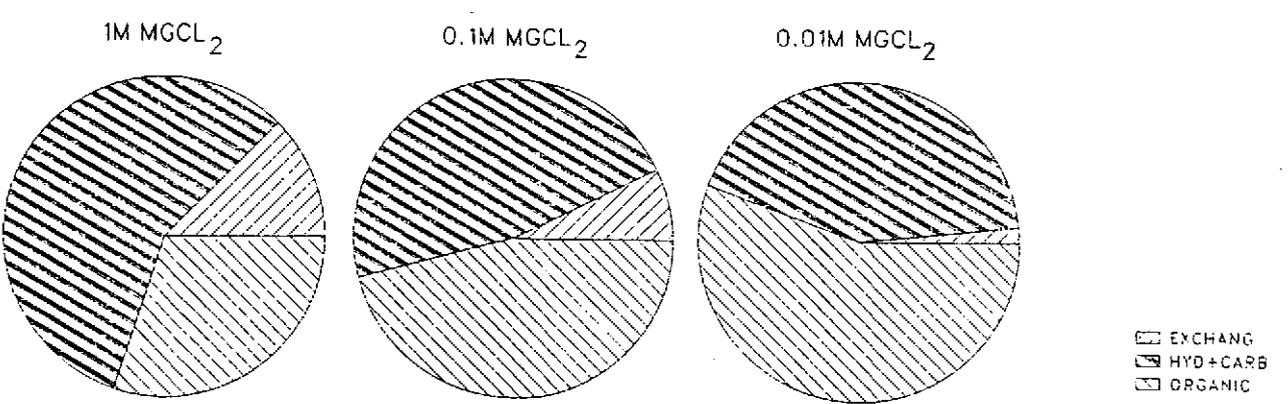


Figure 4.6 Stormwater Solid Metal Extraction, Variation of  $MgCl_2$  Concentration.

The use of 1M MgCl<sub>2</sub> as the extractant gives an indication of the effect of severe snowmelt conditions containing a significant ionic strength. The use of only 0.1M MgCl<sub>2</sub> would not reveal the large amount of Pb which can be easily released from urban sediments under certain conditions. The results also show that it is important to standardise the extractant used. To represent those metals which can be easily released from stormwater solids, 1M MgCl<sub>2</sub> was therefore chosen.

The residual, Carbonate and Hydrous Metal Oxide and Organic, fractions indicate the origin of the Exchangeable metal (Figure 4.5). Most of the Zn comes from the Organic fraction and extraction with 1M MgCl<sub>2</sub> actually leads to an increase of the Carbonate and Hydrous Metal Oxide fraction. Lead, on the contrary, originates from the Carbonate and Hydrous Metal Oxide fraction for 0.01M and 0.1M MgCl<sub>2</sub> extractions, but the Organic fraction is also liberated by 1M MgCl<sub>2</sub>. Copper and Cd are largely derived from the Organic fraction suggesting the presence of surface associated organically complexed species.

#### 4.4.2.2 Efficiency of Hydrous Fe and Mn Oxide Dissolution by Acidic Hydroxylamine Hydrochloride Digestion.

The efficiency of this extraction process was tested by determining the concentrations of Fe and Mn in stormwater suspended solids, both before and after treatment with hydroxylamine hydrochloride. The results are presented in Table 4.2 and show that approximately 98% of both Fe and Mn are liberated by the acidic hydroxylamine hydrochloride extraction method. This method is therefore extremely suitable for releasing hydrous metal oxide associated metals from sediments, and has little effect on organically bound metals, as would be expected.

Table 4.2 Fe and Mn Removal by Extractants.

% Extraction of Fe and Mn		
	Carbonate and Hydrous Metal Oxide Fraction	Organic Fraction
Iron	97.7	2.3
Manganese	98.2	1.8

4.4.2.3 Efficiency of different Methods for breaking down Organic Compounds.

Tessier et al. (1979) have proposed an extraction of "organically" bound heavy metals in sediments by digestion with  $H_2O_2/HNO_3$  at pH 2.0. To assess the efficiency of this, as well as other extraction methods, an experiment was carried out to determine the preferred method of partitioning organically associated heavy metals in stormwater particulates.

The method employed for organic carbon analysis was that of the U.K. Soil Survey (1974) which utilises an acid dichromate oxidation procedure to convert organic carbon to  $CO_2$ . A back titration against ammonium ferrous sulphate allows sample determination when barium diphenylamine p-sulphonate is the indicator.

All analyses were carried out on the  $< 63 \mu m$  fraction of a road dust sample collected from the A41, Hendon, N.W. London, during the Autumn, 1982. This road sediment fraction is thought to be of similar organic composition to the suspended solids found in stormwater.

Sub-samples (1g) of the road dust were treated with extraction/digestion reagents to test their efficiency for organic

carbon removal. Organic carbon analysis was carried out on the residue and the procedure duplicated (Table 4.3).

Table 4.3 Extraction Efficiency of Chemicals used for Fractionating Sediments.

Extractant	% Organic Carbon in Sample after Treatment.	% of Organic Carbon Removed.
None	7.95	
1M MgCl <sub>2</sub> at pH 7.0	7.6	5.4
Acidic NH <sub>2</sub> OH.HCl, 96°C	8.3	0.0
30% H <sub>2</sub> O <sub>2</sub> /0.02M HNO <sub>3</sub> , 96°C	3.5	56.0
0.1M NaOH, 96°C	5.3	33.0
Concentrated HNO <sub>3</sub>	3.5	56.0
Concentrated HNO <sub>3</sub> /HClO <sub>4</sub>	0.6	92.3

The extractants used in earlier stages of the suspended solids speciation scheme showed negligible breakdown of organic material.

The H<sub>2</sub>O<sub>2</sub>/HNO<sub>3</sub> extraction for organically associated heavy metals is commonly used in sequential sediment extraction schemes and yet only removes on average 56% of the total organic carbon. The term "organic fraction" for this digestion procedure may be a misnomer depending upon whether the heavy metals are associated with weakly or strongly bound organic ligands. If, as is probably the case, the remaining 44% of organic material contains at least an equivalent proportion of heavy metals, the results quoted in the literature using this extraction scheme are a considerable under-estimation.

0.1M NaOH gave a 33% extraction of organic carbon which will be composed mainly of humic acid and fulvic acid type materials.

Concentrated  $\text{HNO}_3$  would be preferred to the use of a  $\text{HNO}_3/\text{HClO}_4$  mixture for safety reasons and for more realistic comparison with previous heavy metal values quoted in the literature. However only 56% of organic compounds were oxidised by nitric acid.

The nitric/perchloric acid method, commonly used in the Middlesex Polytechnic Urban Pollution Research Centre, is the most effective of the tested methods with a 92% organics removal efficiency. Strong oxidation procedures have not been incorporated into recent sequential schemes due to the possibility of crystal lattice decomposition, resulting in the release of residual metals. However in polluted sediments only a very small percentage of heavy metals are lithogenic and therefore it is more realistic to risk alteration of this phase rather than partly destroy organic carbon which may be associated with high concentrations of heavy metals.

#### 4.5 Precision of the Speciation Scheme.

During preliminary work the precision of the analysis was determined for all metals and their fractions by triplicate analysis on a bulked sample. The standard deviations obtained are shown in Table 4.4.

In the dissolved phase the fractions are always better than +/- 20% for all metals. This compares favourably with the precision found by Figura and McDuffie (1980) who found batch Chelex extraction to give a precision of better than +/- 25%, and the Electrochemically Available fraction better than +/- 50%. The Electrochemically Available fraction often shows a poor precision compared to the other dissolved fractions which may be related to interferences during the standard addition method by weak organic and inorganic complexation.

Table 4.4 Standard Deviations of the Metal Analysis for Speciating Stormwater.

		Standard Deviation %			
		Zinc	Cadmium	Lead	Copper
Dissolved	Elec. Avail.	15.8	7.0	15.4	-
	Chel. Rem.	18.5	15.1	2.0	12.4
	Tot. Diss.	8.9	4.7	15.2	7.5
Suspended	Exchangeable	11.2	4.3	5.7	5.5
Solid	Carb + Hyd	6.2	-	4.5	8.0
	Organic	21.8	12.5	18.9	6.8

Elec. Avail. = Electrochemically Available  
 Chel. Rem. = Chelex Removeable  
 Tot. Diss. = Total Dissolved  
 Carb + Hyd = Carbonate and Hydrous Metal Oxide

Other work has found better precision for dissolved metal speciation with +/- 5-10% reported by Batley and Florence (1976) and better than +/- 8% by Hart (1980). Batley and Florence found that fractions calculated by the subtraction of measured fractions were only precise to +/- 10-15%. A poorer precision would therefore also be expected for the Strongly Bound fraction, which is the result of subtracting the Total Dissolved and Chelex Removeable fractions.

Most of the deviation found in Table 4.4 can be related to pre-analysis random contamination and losses (e.g. adsorption to container walls), as ASV analysis was found to be precise to better than +/- 5%.

The precision of suspended solid associated metal fractions was generally better than for the dissolved phase. The Exchangeable and Carbonate and Hydrous Metal Oxide fractions were within the better than +/- 10% precision reported by Tessier et al. (1979). However, the Organic fraction shows a lower precision which can be related to a compounding of errors in the sequential extraction scheme.

The speciation scheme has a precision comparable with other similar metal species analysis schemes and provides meaningful data within the deviations in Table 4.4.

#### 4.6. Metal Speciation Scheme Blank Values.

The blank values obtained for the metal speciation scheme are shown in Table 4.5.

Table 4.5 Blank Values for the Metal Species Analysis in Stormwater.

	Blank Concentration µg/l			
	Zinc	Cadmium	Lead	Copper
Elec. Avail.	nd	nd	nd	nd
Chel. Rem.	1.8	nd	1.5	0.4
Tot. Diss.	2.9	0.12	1.3	2.0
Exchangeable	0.3	0.01	0.06	0.06
Carb + Hyd	0.7	0.04	0.14	0.25
Organic	1.0	0.02	0.07	0.2

nd = not detected

The Electrochemically Available blank, obtained by the filtration of water through an acid-washed Nucleopore 0.4  $\mu\text{m}$  filter gave a blank value too low for detection by ASV. However, Hart (1980) used a similar procedure and found blank values of 0.62  $\mu\text{g Zn/l}$ , 0.017  $\mu\text{g Cd/l}$ , 0.11  $\mu\text{g Pb/l}$  and 0.2  $\mu\text{g Cu/l}$ . using Graphite Furnace Atomic Absorption.

The blank values were mostly a direct result of added reagents, i.e. 2M sodium acetate, 1M  $\text{MgCl}_2$  and 0.04M hydroxylamine hydrochloride. These can be significantly purified by passage through a column of Ca Chelex. 2M sodium acetate can be purified by adding 200 mg Ca Chelex to a volumetric flask of the reagent (500 ml) and allowing equilibration. These procedures were only carried out where low detection limits were required, e.g. rainfall analysis. This was usually not a necessity due to the high metal pollution found in stormwater. Concentrated nitric and perchloric acids were always of the highest quality, e.g. BDH-Aristar, and contributed negligible quantities of heavy metals to the blank.

The total dissolved blank corresponds to those reported for the comparable digestion and analysis procedure of Figura and McDuffie (1980). They found blank levels of 0.08  $\mu\text{g Cd/l}$ , 0.6  $\mu\text{g Cu/l}$  and 1.1  $\mu\text{g Zn/l}$ , which were lower due to a further water dilution process.

## CHAPTER 5 INVESTIGATION OF TECHNIQUES WHICH IMITATE BIOAVAILABLE METAL UPTAKE.

The development of a speciation scheme for separating stormwater metal fractions provides some estimation of bioavailable species. An attempt to further improve and refine bioavailable metal determination methods was continued throughout the project. The major direction of this work has been based on the ability of chelating resins to remove metals by a process which imitates metal uptake at the cell surface (Florence 1982b). This is known as the Fundamental Approach (Batley 1983). The use of chelating resins in this respect was reviewed in Section 2.4.1.

Chelex-100 which possesses carboxylic acid and amine functional groups, as well as possessing a porous structure, was the first resin used by workers to select bioavailable metals (Florence and Batley 1980). However the sulphur containing compounds of biota, such as metallothioneins or amino acids, may react in a different way to heavy metal species than do the Chelex-100 ligands. Florence (1982b), therefore, used resins containing thiol ligands to imitate the metal binding protein, metallothionein.

Unlike metallothionein, cysteine is an amino acid known to be ubiquitous amongst biological cells and also contains the thiol functional group. If a cysteine resin could be prepared then its use may represent a useful medium for the detection and removal of bioavailable metals from polluted waters.

The transport of metal species across the biological membrane may not be directly comparable to resin kinetics; in fact membrane transport is a slow process (Turner 1983). It is not surprising therefore that a thiol resin was found to over-estimate the toxicity of metal species towards algae in seawater (Florence et al. 1983).

It would therefore also be interesting to attempt to imitate the function of the cell membrane in addition to the cell constituents.

Dialysis provides a suitable analytical method to imitate the functional cell membrane barrier and, while developing cation exchange dialysis, Cox et al. (1984) have shown that it is possible to collect (in receiving electrolytes) metal species which have traversed the dialysis membrane from a sample solution.

If a receiver could be encapsulated in a dialysis bag and placed in the stormwater outfall water for several days, then the resulting metal taken up may represent an assessment of potential biological uptake. A cysteine resin would then constitute a suitable receiver for selecting bioavailable metal species. In addition the dialysis membrane pore size and resin diameter can be selected so that the resin remains in the dialysis bag.

The method described in outline above can be termed *Dialysis with Receiving Resins*. If the surface area of the dialysis bag is known then the transfer of the pollutant into the model dialysis cell can be expressed in terms of a metal uptake rate per unit surface area. The method should be particularly suitable for long term sampling where sporadic flushes of metals are experienced. These may be missed by sampling procedures, but are not missed by the continuously monitoring *Dialysis with Receiving Resins* approach.

However, there may be some problems in interpreting the results from this analytical technique;

a) Although metal transport across the cell membrane is primarily controlled by diffusion - which is the same process as *Dialysis with Receiving Resins* - the dialysis membrane is only a substitute for a real membrane. The latter could be prepared by membrane mimetic chemistry where phospholipids are converted to suitable liposomes (Fendler 1984). It would then be necessary to find methods of either

- i) entrapping suitable thiol groups in the prepared double layer vesicle bags
- or ii) generating thiol groups *in situ* from precursors
- or iii) selecting phospholipids already containing thiol groups in the hydrocarbon bilayers.

- b) The chelating resin does not fill the dialysis bag. A chelating gel, such as that prepared by Culberson et al. (1982), could be used to fill the bag and provide an improved diffusion gradient.
- c) *Dialysis with Receiving Resins* only provides a measurement of potential bioavailable metal uptake. No detailed information, as provided by the speciation scheme described in Chapter 4, on the variations of metal species through storm and snowmelt events is provided.

The aim of the work described in this Chapter was to develop a procedure suitable for analysing bioavailable heavy metal species in stormwater. In order to prepare a suitable cysteine chelating resin for the removal of bioavailable heavy metal species from stormwater samples, and for encapsulation in dialysis bags, two experimental synthetic procedures were carried out.

#### 5.1 Preparation of Cysteine Chelating Resin I.

Liu and Sun (1981) have described the preparation of a cysteine chelating resin based on a macroporous cross-linked polyacrylonitrile co-polymer, in which the cysteine molecules are bound to a carboxylic acid form of the polymer by esterification. A major problem with this synthetic scheme is that the starting co-polymer is not commercially available and preliminary experiments carried out in this study demonstrated the difficulties associated with its preparation. In particular the polymerisation step was difficult to control successfully.

An alternative starting material is a commonly available macroporous resin (e.g. Amberlite XAD-4) prepared from divinylbenzene and which ~~can be converted to a carboxylic form (Meyers and Fritz 1976).~~ This intermediate can then be converted to an amino acid chelating resin according to the esterification method of Liu and Sun (1981).

The synthetic scheme is shown in Figure 5.1. It should be noted that in the final product the free carboxylic acid group of the cysteine is

bound as an ester linkage. The available metal chelating groups are therefore amine and sulphhydryl groups. However, it is possible that there may be unreacted carboxyl groups remaining on the XAD-4 resin (Phillips and Fritz 1978).

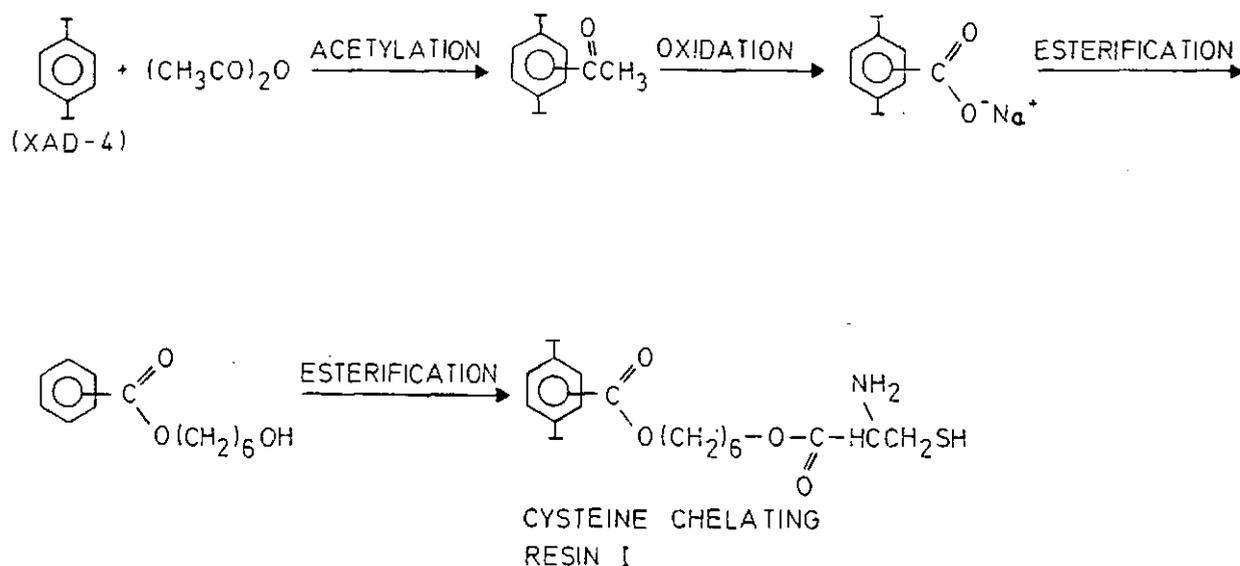


Figure 5.1 Synthesis Scheme for Preparing Cysteine Chelating Resin I.

#### 5.1.1 Method of Preparation.

Commercial XAD-4 resin was ground and sieved to either 63-250  $\mu\text{m}$  (Batch 1) or 106-250  $\mu\text{m}$  (Batches 2 and 3). The higher proportion of fines in Batch 1 created difficulties when transferring the resin into a chromatography column during the metal extraction experiments. This problem was removed for Batches 2 and 3 where particles finer than 106  $\mu\text{m}$  were avoided.

The sieved XAD-4 was cleaned by refluxing with methanol followed by suction filtration. Further washing with 12M hydrochloric acid, water and acetone was necessary before the resin, after drying overnight at 50°C, was ready for use.

To the XAD-4 resin (5g) was added anhydrous aluminium trichloride (35g) and 60-80°C petroleum ether (20 ml). Over a 30-60 minute period a mixture of 50:50 petroleum ether/acetic anhydride (20 ml) was added through a water cooled condenser and the mixture refluxed at 75°C for three hours. The product was cooled to room temperature and hydrolysed in a mixture of 12M hydrochloric acid and ice. After collection by suction filtration the product was washed successively with 15M ammonium hydroxide, 12M hydrochloric acid, water and acetone. The complete procedure was repeated to obtain a higher yield of the acetylated product, which was dried at 50°C.

The acetylated product was oxidised to the carboxylic acid intermediate by stirring for one hour with 0.1M potassium permanganate in 2% sodium hydroxide. The product was collected, washed and dried as for the acetylated intermediate.

The carboxylic acid resin was then mixed with molten 1,6-hexanediol (30g) containing 18M sulphuric acid as a catalyst. Under these conditions the esterification was completed by reacting at 70°C for 24 hours. The product was washed with boiling methanol and dried (50°C).

The resulting resin was added to a mixture of L-cysteine (30g), dioxane (50 ml) and 18M sulphuric acid (2 ml), and heated at 90°C for 24 hours. The final product was washed with water, 12M hydrochloric acid, water and acetone. After drying at 50°C the collected product was a tan colour.

#### 5.1.2 Potentiometric Titration of Cysteine Chelating Resin I.

In this type of titration the acidic groups on the resin are ~~neutralised by a base. The pH at the volume for half neutralisation of~~ a particular acidic group is equivalent to the  $pK_a$  value.

Other workers have reported results for the potentiometric titration of chelating resins, as shown in Table 5.1, but it is difficult to test the authenticity of their data. In both cases the prepared resin

was known to contain unreacted carboxylic acid groups. The assigned  $pK_a$  values for the carboxylic acid groups seem high compared to normally quoted  $pK_a$  values.

Table 5.1 Potentiometric Titration Results for Metal Chelating Resins.

Reference	Resin	Chelating Group	Reported $pK_a$	Normally Quoted $pK_a$
Moyers and Fritz (1976)	Hexylthioglycolate	-COOH	4.40	1.86
		-SH	7.90	10.34
Liu and Sun (1981)	Cysteine	-COOH	5.65	1.86
		-NH <sub>3</sub> <sup>+</sup>	6.59	8.35
		-SH	7.16	10.34

Liu and Sun (1981) do not show the titration curve from which their data is derived, and the graph presented by Moyers and Fritz (1976) does not allow the easy interpretation they suggest.

#### 5.1.2.1 Potentiometric Titration Method.

The resin (0.2g) was equilibrated with water (50 ml) through which a stream of nitrogen gas was passed. Titration against 0.1M sodium hydroxide was carried out, using a pH electrode to follow the progress of the reaction. Small increments (0.04-0.1 ml) were added with a five minute equilibration time between each addition.

#### 5.1.2.2 Results for the Potentiometric Titration.

The typical titration curve obtained for Cysteine Chelating Resin I is shown in Figure 5.2. The isoelectric point, where the dipolar ion exists, occurs at pH 4.2. A neutralisation process commences at pH 8.9

and is still occurring after the addition of 1.5 ml of 0.1M NaOH. This can be attributed to the neutralisation of the protonated amine group.

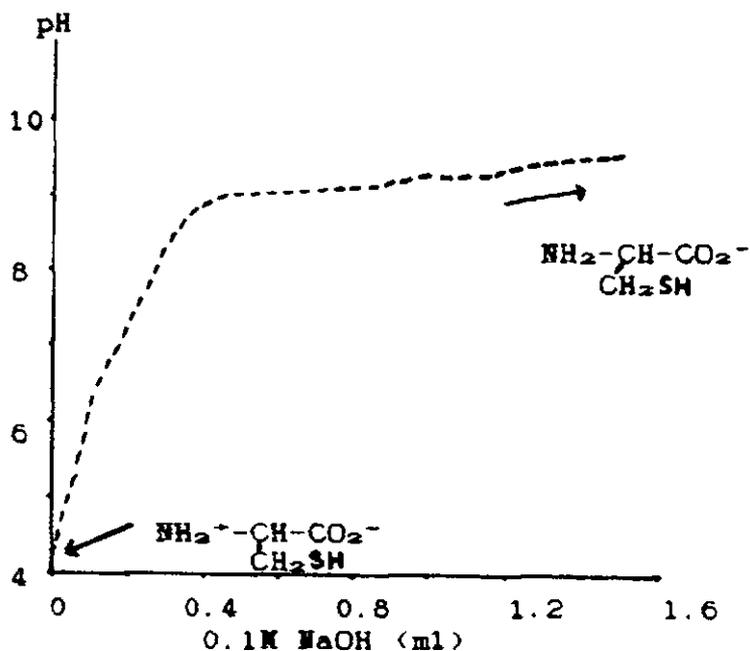


Figure 5.2 Potentiometric Titration for Cysteine Chelating Resin I (0.19 g).

### 5.1.3 Infra-red Analysis of Cysteine Chelating Resin I.

The infra-red spectrum of the resin in a KBr pellet was recorded. When the spectrum is compared to that of XAD-4, new bands can be seen to have appeared at 1679, 1348 and 1262  $\text{cm}^{-1}$ . The 1262 and 1679  $\text{cm}^{-1}$  bands may represent carbonyl (C=O) linkages within either of the two ester groups in the molecule (Figure 5.1).

### 5.1.4 Mass Spectrum of Cysteine Chelating Resin I.

The resin was ground to a fine powder and a small amount (0.01g) introduced, via a direct insertion probe, into a Hewlett Packard Model

5995B, Gas Chromatograph/Mass Spectrometer. Individual functional groups were not found, although a great abundance of elemental sulphur was detected. The presence of sulphur suggests that the attachment of cysteine to the prepared resin has been successful.

#### 5.1.5 Heavy Metal Chelating Capacity of Cysteine Resin I.

The batch chelating capacity for Zn, Cd, Pb and Cu was determined as described below.

##### 5.1.5.1 Technique for the Determination of Batch Capacity.

The metal standard (30 ml), at a concentration of 1 mg/ml, was adjusted to the required pH with 0.1M sodium hydroxide solution. Cysteine Chelating Resin I was added and the mixture equilibrated for two hours. The resin was transferred into a chromatographic column and washed with water. The metal bound to the resin was eluted with 1M nitric acid (10 ml) and, after making up to volume (25 ml), the metal concentration was determined by ASV.

##### 5.1.5.2 Results for the Batch Capacity.

When the pH of the metal standards was adjusted to 7.0 it was observed that Cu and Pb precipitated as hydroxide, because of this problem the Zn and Cd results were also not considered reliable.

The batch capacity determination was therefore carried out at pH 4.0, at which point the metal hydroxides are soluble. The metal uptake capacity for chelating resins is greatly increased at higher pH values (Culberson et al. 1982) and therefore the values obtained should be considered as minimum capacities under stormwater conditions.

The batch capacity results for the resin at pH 4.0 are shown in Table 5.2. Copper shows the greatest affinity for the resin, followed by Zn and Cd, with Pb having the lowest affinity. This order is similar to that of Chelex-100 which has an order of selectivity of Cu > Pb > Zn >

Cd (Bio-Rad 1981). The uptake capacity of Cu is similar to that found by Culberson et al. (1982) for their chelating gel.

Table 5.2 Batch Capacities for Cysteine Chelating Resin I (pH 4.0).

	$\mu\text{g/g Resin}$	$\mu\text{mol/g Resin}$
Zinc	567.5	8.68
Cadmium	948.8	8.44
Lead	974.4	4.7
Copper	944.5	14.86

### 5.2 Preparation of Cysteine Chelating Resin II.

A second synthesis was attempted by an alternative route which reduced the preparation time from one week to two days; in addition the hydroxymethyl intermediate is recognised as a better product, containing fewer free carboxylic acid groups (Phillips and Fritz 1978).

The synthesis involves the same starting resin as resin I (XAD-4) but differs in that the esterification with cysteine involves an hydroxymethyl intermediate (Figure 5.3). The synthesis also involves fewer procedural steps.

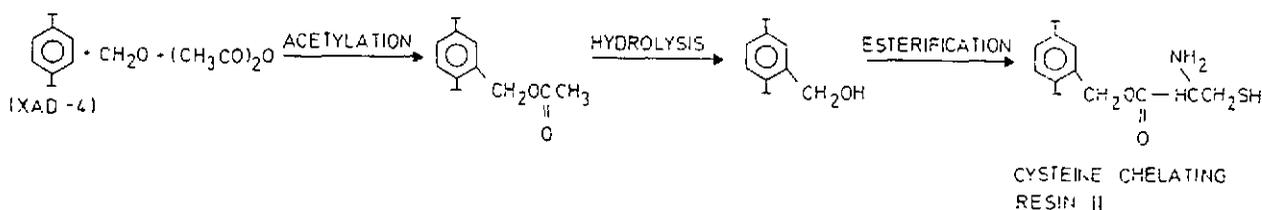


Figure 5.3 Synthesis Scheme for preparing Cysteine Chelating Resin II.

### 5.2.1 Method of Preparation.

In this synthesis XAD-4 was ground and sieved to 125-250  $\mu\text{m}$ , followed by rinsing with methanol. After drying overnight (50°C) the XAD-4 (15g) was mixed with paraformaldehyde (3g), acetic acid (40 ml) and acetic anhydride (10 ml) using magnetic stirring. After a few minutes zinc chloride (15 g) was added and the flask secured. Heating overnight at 60°C produced the acetoxymethyl intermediate which was rinsed with methanol and isolated by suction filtration.

The resulting resin was hydrolysed by refluxing with concentrated hydrochloric acid and methanol (1:9 v/v) for one hour. The hydroxymethyl intermediate was isolated by suction filtration and dried overnight (50°C).

To a portion of the product (7.5g) was added dioxane (75 ml), concentrated sulphuric acid (4 ml) and L-cysteine (45g). After thorough mixing with a magnetic stirrer the mixture was heated overnight in a stoppered flask at 70°C. The cysteine resin was isolated by suction filtration and washed with water, concentrated hydrochloric acid, methanol and finally water. The product was dried overnight (50°C).

### 5.2.2 Potentiometric Titration for Cysteine Chelating Resin II.

Potentiometric titrations, by the method described in Section 5.1.2.1, were carried out for the intermediates, as well as the final product, Cysteine Chelating Resin II.

XAD-4 was not found to contain any acidic groups. However, for both the acetoxymethyl and hydroxymethyl intermediates an acidic group was present ( $\text{pK}_a = 2.83$ ) which cannot be explained theoretically by the synthesis scheme (Figure 5.3). It is possible that the reagents used during the first stage of the synthesis may result in a carboxylic acid group being attached to the XAD-4 starting resin. The acidic group remains unaffected during the hydrolysis step.

The comparison of the potentiometric titration curves for the Cysteine Chelating Resin II and pure cysteine reveals a close similarity between the two (Figure 5:4), except that for the former the isoelectric point occurs at a lower pH value. This can only be due to the presence of unreacted acid groups on the resin as the carboxylic acid group on the cysteine resin is bound as an ester and therefore does not contribute to the titration curve.

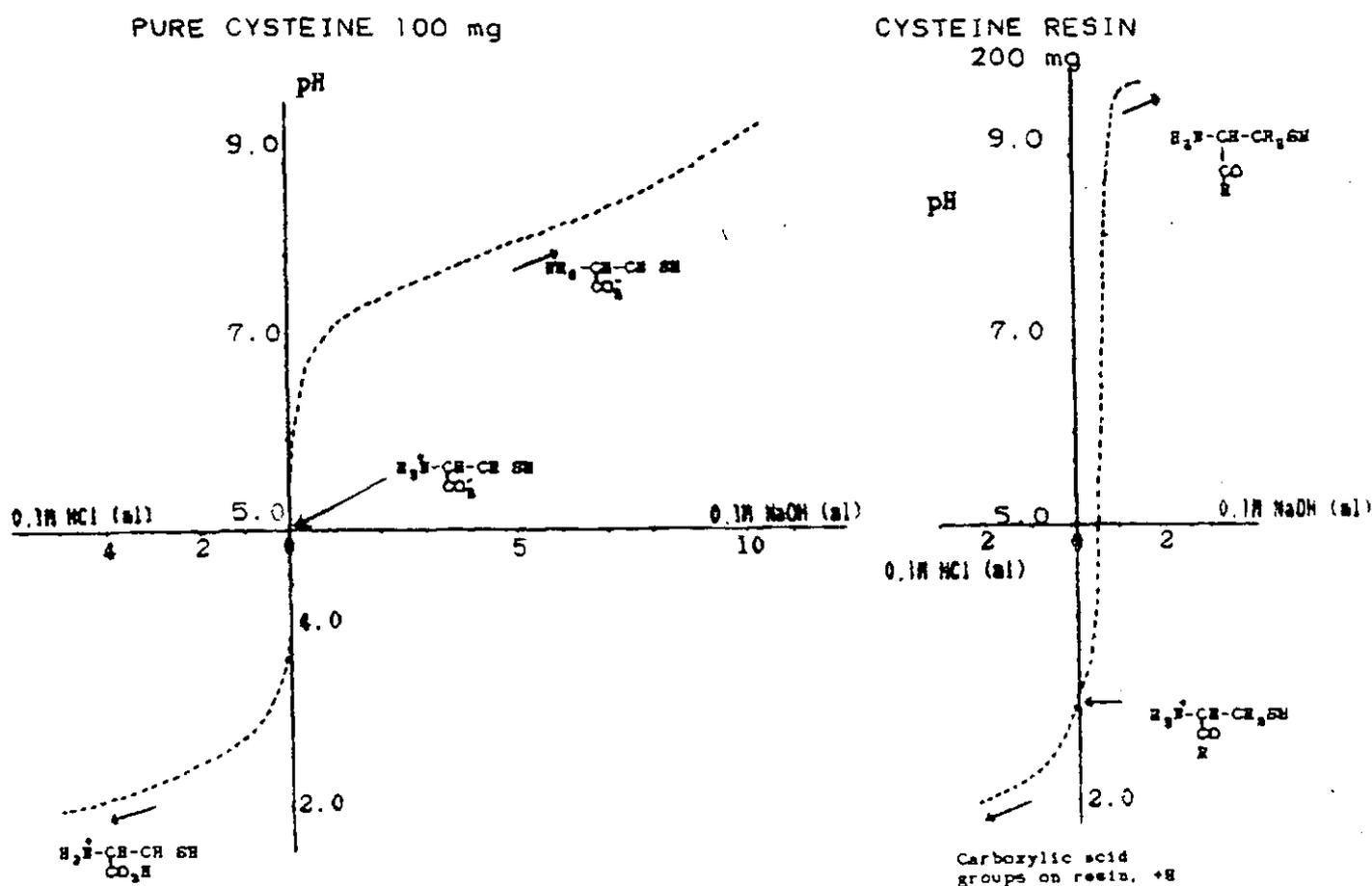


Figure 5.4 Comparison of Potentiometric Titration Curves for Pure L-cysteine (100 mg) and Cysteine Chelating Resin II (200 mg).

### 5.2.3 Infra-red Analysis of Cysteine Chelating Resin II.

The infra-red spectra of Cysteine Chelating Resin II and its intermediates revealed peaks at 1740 and 1240  $\text{cm}^{-1}$ , which can be attributed to C=O and C-O stretching vibrations respectively. These peaks were absent from the XAD-4 starting material and the hydroxymethyl derivative, which supports the structures shown in Figure 5.3.

### 5.3 Preparation of a Chelating Resin Containing Thiol Groups.

The use of a resin containing thiol groups to imitate the role of metallothioneins in metal uptake was first applied to metal speciation studies by Florence (1982b). In this study the thiol resin was prepared for a comparison of bioavailable metal uptake with the cysteine chelating resins (Figure 5.5).

The hydroxymethyl XAD-4 intermediate of Phillips and Fritz (1973) was prepared following the procedure outlined in Section 5.2 and the thiol group attached by esterification with thioglycollic acid (Phillips and Fritz 1978).

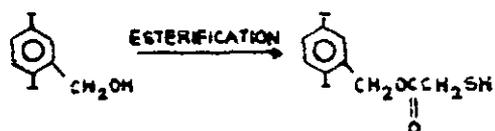


Figure 5.5 Synthesis Scheme for Preparing Thiol Resin.

#### 5.3.1 Method of Preparation.

The hydroxymethyl intermediate (10g), prepared as described in Section 5.2, was reacted overnight with thioglycollic acid (40 ml) and concentrated hydrochloric acid (2 ml), under a stream of nitrogen, at 60°C. After isolating the product by suction filtration, followed by

successive washing with water, concentrated hydrochloric acid and methanol, the final product was dried at 50°C.

#### 5.4 Comparison of Cysteine, Chelex-100 and Thiol Chelating Resins for the Uptake of Metals from a Stormwater Sample.

The suitability of different chelating resins for removing bioavailable metal species from stormwater may be assessed by comparing metal species uptake by each resin from a sample. Florence (1982b) has compared Electrochemically Available, Chelex Resin Removeable and Thiol Resin Removeable heavy metals in seawater, tap water and creek water samples. Only the column method was used for resin extraction, while in the present work a batch method was used to provide a complete equilibration of the resin with the sample. The important results obtained by Florence (1982b) were;

- a) the Thiol resin extracts more Cu than Chelex-100.
- b) Electrochemically Available metal was higher than Thiol Removeable for Cd and Pb, but the reverse for Zn and Cu.
- c) in some cases Cd and Pb, although Electrochemically Available, showed zero adsorption on Chelex-100 and Thiol resins.

In this study a similar comparison, using both column and batch methods, was made for the uptake of metal species by different chelating resins from the dissolved phase of a stormwater sample.

##### 5.4.1 Methods for Metal Analysis.

The Electrochemically Available, Total Dissolved and Chelex Removeable (batch) metals were determined as described in Section 4.1. Column extraction was accomplished using a 4 cm bed depth of resin, contained in a small chromatography column (diameter, 1 cm). The sample (50 ml) was passed slowly through the column and the retained metal was eluted with 1M HNO<sub>3</sub> (10 ml) followed by washing with water (10 ml). After making up to volume (25 ml) the metal levels in the eluate (7 ml) were determined by ASV after the addition of 2M sodium acetate (3 ml). Batch extraction for the Thiol and Cysteine resins was carried out as

described in Section 4.1 for Chelex-100, except that any pre-analysis resin preparation was omitted.

#### 5.4.2 Results for a Preliminary Sample.

A bulked sample (2 l) of stormwater from the Oxhey catchment, which had been frozen, was filtered and analysed (in duplicate) for Electrochemically Available, Total Dissolved and Thiol, Chelex and Cysteine Removeable metals. The results are expressed in a bar chart form (Figure 5.6).

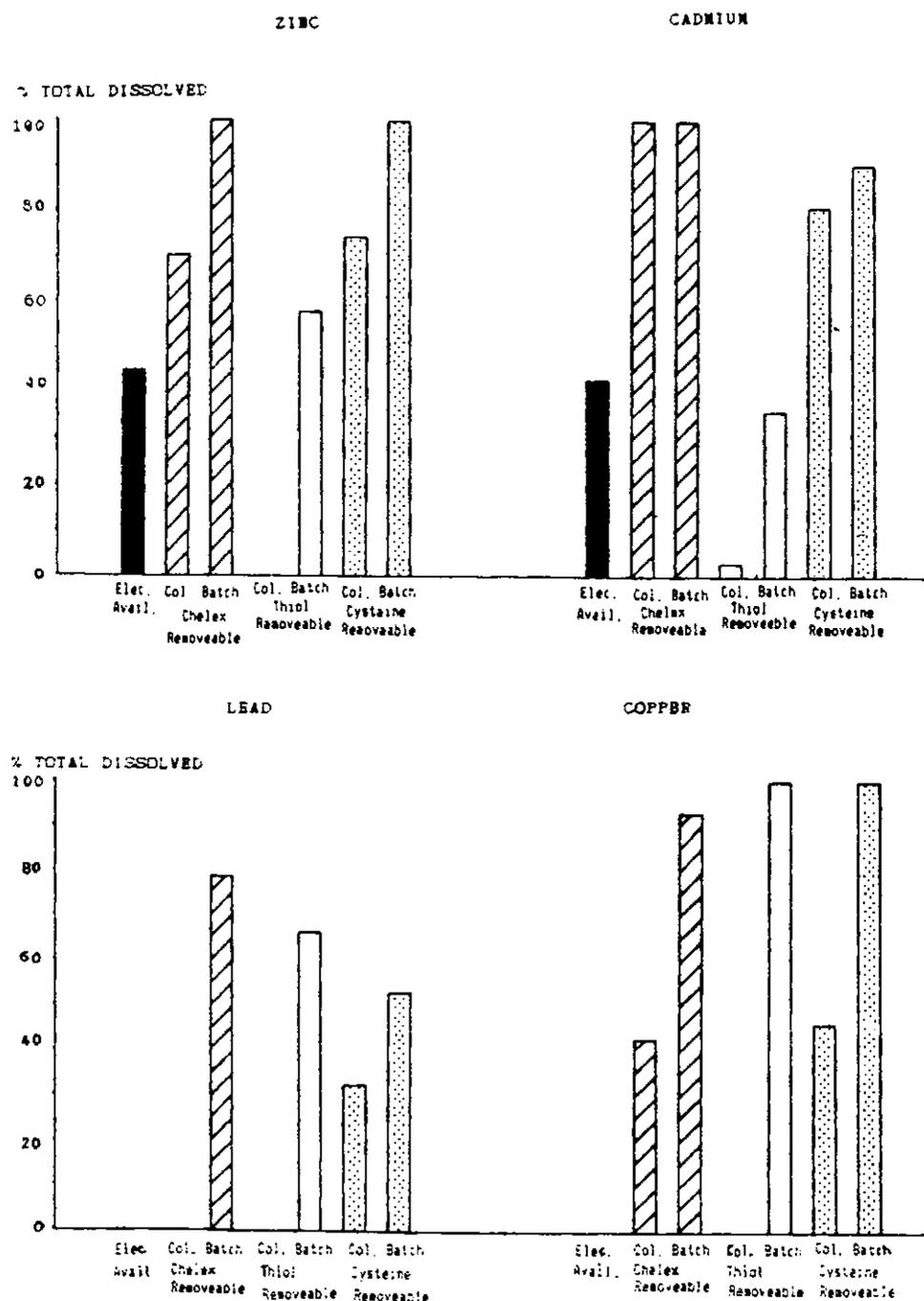


Figure 5.6 Comparison of Uptake of Metals from the Dissolved Phase of a Stormwater Sample by Different Chelating Resins.

There is a consistently higher removal by batch, as compared to column, methods for dissolved metal species. This can be attributed to the non-equilibration of the column method and therefore incomplete metal uptake. In some cases, especially with Cysteine resin and Chelex resin batch methods, 100% removal of metal species is occurring. This is not so obvious in the case of Pb, probably due to the formation of strongly bound complexes.

There is a close similarity in the affinities of Zn and Cd for the different resins. This suggests that these two metals may exist as similar metal species. Another interesting feature is that the Thiol column method nearly always produces zero extraction. The metal species are therefore not labile to thiol over the timescale of the column contact.

In the case of the Thiol batch method the metal species are more responsive, particularly for Cu, and to a lesser extent the other three metals. The Thiol results are generally comparable with the findings of Florence (1982b).

For all four metals there is a marked similarity of extraction efficiency between the Chelex and Cysteine resins, particularly in the case of Zn and Cu. In terms of the Fundamental Approach this demonstrates that Chelex-100 can be fairly representative of metals taken up by cell structures, although the Cysteine resin is preferred, as the sulphur chelating groups may be more typical of the metal chelating groups found in biota. The major difference between the two resins occurs in the case of Pb, where Chelex-100 is more efficient, but otherwise the resins seem to behave similarly and give identical interpretations in terms of bioavailable metals.

#### 5.5 Dialysis with Receiving Resins.

If the cell constituents can be imitated by uptake of metal species onto an amino acid chelating resin, then dialysis may reasonably imitate the function of a cell membrane. Although high concentrations

of bioavailable heavy metals may exist in stormwater this does not necessarily mean that they are bio-assimilated. Adsorption of metal species to the cell membrane is known to be fast, relative to transport across the cell membrane (Mouvet 1984). If the adsorbed species are removed after a storm event, when baseflow conditions are dominant, then the membrane transfer process may not be rapid enough for the organism to be affected by the metal levels present in the stormwater.

Dialysis membranes, prepared from cellulose and with a molecular weight cut-off value of 1000, are available. They may imitate quite closely the response of a cell membrane to metal species, although it should be remembered that a true cell membrane has a phospholipid structure. In addition the state and species of the organism will affect metal transport. By incorporating the Cysteine resin into a dialysis bag and locating this at the stormwater outfall, a simulation of metal species-organism interaction can be achieved.

#### 5.5.1 Method for Dialysis with Receiving Resins.

Spectrapor wet dialysis tubing with a molecular weight cut-off value of 1000, and a tube diameter of 47 mm, was used. This had been conditioned and metal contamination removed by equilibration in water and Chelex-100 (100 mg) respectively overnight. A bag length of 60-100 mm was found to be suitable and was accurately measured. The resin (200 mg) was slurried with water ( $\approx$  20 ml) into a dialysis bag. After tightly sealing the bag at both ends it was suspended in the stormwater outfall for a period of 3-4 days.

On return to the laboratory the dialysis bag was cut open and the resin released into a separating column and washed with water (10 ml). The resin was then eluted with 1M HNO<sub>3</sub> (10 ml) and water (10 ml) and analysed for heavy metals as described for Chelex in Section 4.1.

### 5.5.2 Results for two Preliminary Measurements.

A preliminary study of the method was carried out at the Bergsjön field station (see Section 3.2). However, Chelex resin together with dialysis tubing, which had a molecular cut-off value of 3500, was used for this test.

Uptake of metals should be dependent on the exposed surface area (see Section 5.5.3), and therefore the heavy metals retrieved by the resin are expressed as an uptake rate, in ng of heavy metal/mm<sup>2</sup> of dialysis membrane surface area/hour, as shown in Table 5.3.

Table 5.3 Uptake of Metals by Chelex-100 in a 3500 Molecular Weight Cut-off Dialysis Bag.

Time Period	Metal Uptake Rate, ng/mm <sup>2</sup> /hour			
	Zinc	Cadmium	Lead	Copper
10.00, 22.11.84 to 15.00, 26.11.84	73.1	0.12	0.51	19.3
15.00, 26.11.84 to 11.00, 29.11.84	26.5	0.05	0.25	2.03

The first and second time periods had runoff volumes of 650.4 and 169.2 m<sup>3</sup> respectively. All four metals show increased metal uptake during the first period. It seems therefore that *Dialysis with Receiving Resins* is sensitive to increased intermittent stormwater discharges.

5.5.3 Relationship between Dialysis with Receiving Resins Metal Uptake and Surface Area.

The uptake of metal into the dialysis cell would be expected to be related to the surface area of the exposed membrane. It is important to find out if this relationship holds so that the results can be expressed as an uptake rate per unit surface area.

Five dialysis bags, of different sizes, with a molecular weight cut-off value of 1000 and containing the Cysteine resin, were placed at the Bergsjön stormwater outfall during a snowmelt period (21.02.85 to 25.02.85). The results in Table 5.4 give the uptake rate in pg/mm<sup>2</sup>/hour for each metal.

Table 5.4 Metal Uptake Rate for *Dialysis with Receiving Resins* depending on Surface Area.

Surface Area mm <sup>2</sup>	Metal Uptake Rate, pg/mm <sup>2</sup> /hr			
	Zinc	Cadmium	Lead	Copper
4313	13.3	0.57	0.012	23.7
5391	20.0	0.54	nd	37.1
9165	14.7	0.51	1.14	25.3
9524	21.4	0.50	nd	27.7
13298	15.9	0.53	0.079	22.1
Mean	17.1	0.53	-	27.2
Standard deviation	3.12	0.024	-	5.29
	(+/- 18.3%)	(+/- 4.5%)		(+/- 19.5%)

It is clear that for Zn and Cu, and especially for Cd, a linear relationship exists between metal uptake rate and the membrane surface area. The Pb results are often close to the measured Pb blank value.

The low values of Pb found are related to the low dissolved Pb concentrations found in stormwater, despite a high suspended solid concentration.

The results in Table 5.4 support the theory that the transport of metal across the membrane is by diffusion from a high to a low metal concentration, with the chelating resin regulating the aqueous metal concentration in the dialysis bag close to zero. According to this the metal taken up should be dependent on the dialysis bag surface area, as can be seen in Table 5.4. Table 5.4 also shows that the method is reasonably precise for Zn and Cu and with a good precision for Cd thus allowing the use of the method for routine stormwater monitoring.

## CHAPTER 6 GULLYPOT METAL SPECIATION - MECHANISMS, OUTFLOW LOADINGS AND MASS BALANCES.

The gullypot is a small scale sedimentary basin which regulates, if somewhat inefficiently, highway surface runoff pollution (Harrop 1983). Current knowledge on the fate of heavy metals in gullypots was discussed in Section 2.1.1.3 and certainly the inputs, outputs and interactions within a gullypot with regard to metal speciation have received scant attention to date.

Speciation transformation processes, in this fermenting underground water reservoir, can certainly be anticipated when a rapid change of gullypot contents occurs. This is normally brought about by the shock pulse of acidic, well oxygenated rainfall which enters the system via the road surface. In this chapter processes affecting metal speciation through the rainfall/road surface/gullypot system are investigated by the analysis of data collected during a 2½ month study of the Chalmers catchment (the catchment characteristics are described in Section 3.3). Metal speciation data for atmospheric fallout, size fractionated road dusts, road runoff, gullypot liquor and gullypot outflow allowed the observation of six physical and chemical processes which affect the transport of metals through the gullypot system. These controlling processes are used to explain metal loading variations for the gullypot outflow and finally mass balances are drawn up for metal species through the system.

It is first necessary to outline and discuss the type of storm samples collected during the study period.

### 6.1 Storm Characteristics.

Six storm events of different flow intensity and volume types were studied. The hydrological characteristics of these events are presented in Table 6.1.

Table 6.1 Hydrological Characteristics for Six Storm Events Sampled in the Gullypot.

Storm Code	Date	Sample type collected (No. of samples)	Antecedent Dry Period (days)	Storm Duration (hours)	Rainfall (mm)	Road Runoff (litres)
6A	02.07.84	Road runoff (17)	8	2.1	≈10	1689
6B	12.07.84	Road runoff (11) Gullypot (12) Gullypot outflow (12)	10*	5.8	18.5	6932
6C	01.08.84	Gullypot (12) Gullypot outflow (5)	3	8.7	2.9	1667
6D	04.08.84	Road runoff (4) Gullypot (7) Gullypot outflow (6)	1	4.3	4.6	2155
6E	15.08.84	Gullypot (7) Gullypot outflow (7)	10	1.0	9.7	3951
6F	03.09.84	Gullypot (7) Gullypot outflow (6)	1	2.5	6.5	3992

\*0,6 mm rainfall on preceding day

In addition the gullypot continuous monitoring system gave values every minute throughout each storm event for dissolved oxygen concentration, redox potential, conductivity and pH.

Two storm events, 6B and 6E, occurred after relatively long antecedent dry spells. 6E was the most intense storm with 2.7 mm rain falling in a five minute period, although the whole event only lasted one hour. The runoff for this thunderstorm was close to the design capacity of the sewer network (1 l/s on 100 m<sup>2</sup> for 15 minutes) with a maximum flow of 4.6 l/s.

Storm 6B was a long heavy storm which continued for 5.8 hours. It had a maximum road runoff flow rate of 2.03 l/s and the overall flow volume of 6932 litres represented the greatest value for any one event during the 2½ month study period. This storm began with a low flow for the first hour of 0.05 l/s, but had two intense rainfall periods during the third hour. Storm 6A was also an intense summer storm of two hours duration with most of the flow volume occurring during the first half hour. Storms 6C, 6D and 6F were low intensity storms with a short antecedent dry period.

The outflow loadings for four controlling parameters and the dissolved and suspended solid associated metals for five of the storm events, 6B - 6F, are shown in Table 6.2 and can be compared to the hydrological characteristics in Table 6.1. Although only five storms were monitored, dissolved organic carbon loadings (Table 6.2) show a clear positive linear relationship to antecedent dry period (Table 6.1). This suggests a continuous accumulation of organic carbon, available for washout, during the dry period both on the road surface and in the gullypot liquor and sediment. A similar, but weaker, relationship between suspended solids and antecedent dry period is found. This is due to a further dependence on gullypot sediment mobilisation processes. During intense and large volume storm events a net loss of gullypot sediment occurs, while during less intense events the gullypot gains sediment. For suspended solids, the antecedent dry period relates only to road surface sediments so that when the gullypot contribution increases the correlation (suspended solids with antecedent dry period) becomes weaker. The importance of the gullypot for contributing sediment can be seen for storm 6B when the gullypot

produced 66.5% of the suspended solids in the outflow whereas storm 6D contributed only 11.3%.

Table 6.2 Outflow Loadings of Parameters and Heavy Metals for Five Storm Events.

Storm code	Parameter Outflow Loadings (g)				Metal Outflow Loadings (mg)							
	Diss Ca	Diss Org C	Part Org C	Suspended Solids	Zinc		Cadmium		Lead		Copper	
					Diss	SS	Diss	SS	Diss	SS	Diss	SS
6B	12.4	28.3	45.3	467	296	182	2.6	1.0	80	812	123	71
6C	3.9	15.1	2.4	23	268	10	1.2	0.2	49	40	105	9
6D	2.1	10.3	1.5	28	128	7	0.8	0.15	28	48	79	6
6E	2.7	21.4	26.2	314	204	109	2.0	0.7	27	249	99	76
6F	1.6	6.5	7.6	48	198	31	0.9	0.3	17	75	23	9

Diss = Dissolved  
 SS = Suspended Solid  
 Org = Organic  
 Part = Particulate

Metal loadings follow the controlling parameter loadings, such as dissolved organic carbon and suspended solids, through the gullypot system. A good linear positive relationship exists between dissolved organic carbon and all four dissolved metals (Table 6.1 and Table 6.2), but no relationship exists for dissolved Ca. A positive linear relationship also exists between suspended solids and suspended solid associated metals. However, particularly in the case of Zn, a better relationship is obtained by considering particulate organic carbon. This can be accounted for by the enrichment of organic carbon and metals in suspended solids at low flow rates.

## 6.2 Chemical and Physical Processes affecting Metal Species through the Gullypot System.

The processes affecting metal species are assessed by initially considering atmospheric fallout and then following metal transport over the road surface, within the gullypot and thence to the gullypot outflow pipe.

### 6.2.1 Atmospheric Fallout.

Atmospheric fallout is an important source of heavy metals, particularly for dissolved metal species. The importance of combined precipitation and dust fallout for storm 6B is shown in Table 6.3. Although in low concentrations, metal loadings become significant for a large volume storm event.

Table 6.3 Possible Heavy Metal Contribution of Atmospheric Fallout to Road Runoff, Storm 6B.

Atmospheric Fallout Metal as a % of Road Runoff			
	Total metal	Dissolved metal	Solid metal
Zinc	id	id	id
Cadmium	22.2	nd	63.6
Lead	64.5	153.9	42.9
Copper	249.3	316.4	129.9

id = insufficient data  
nd = not detected

In the dissolved phase all the Pb and Cu in the road runoff can be accounted for by atmospheric fallout. Suspended solid fallout is less important for Pb, but could potentially comprise all of the Cu and a considerable amount of the Cd found in the road runoff.

A significant amount of the dissolved metal in the precipitation may result from readily soluble airborne solids. For example, solid associated heavy metals can be rapidly solubilised by the acidic rainfall, which in this storm had a recorded pH of 4.1. The road surface may reduce the transfer of atmospheric fallout to the gullypot due to the immobility of coarser solids and chemical changes in metal speciation during the washoff process. In the case of Pb the abundance of road dust associated metal (e.g. 2556 mg for storm 6A) offsets the relative importance of rainfall solids input (58.6 mg for storm 6A). In fact this is usually true for Cd, Cu and Zn as well.

Atmospheric fallout is also an important source of free dissolved metal species, which is related to the low pH (average 4.2) and low dissolved organic carbon concentration (average 1.3 mg/l). For storm 6B, in atmospheric fallout, 46% of total Cd, 18% of total Pb and 68% of total Cu, was in the Chelex Removeable fraction. These reactive metal species can be readily adsorbed to, or complexed by, organic and inorganic compounds and may not even become a constituent of road runoff.

### 6.2.2 Metal Mobilisation from Road Dusts.

Two processes are known to affect the mobilisation of metals from road dusts. Firstly, the acidic nature of rainfall helps to transfer metal species into the dissolved phase. Secondly, the chemical sorting of metal species takes place over and at the road surface during runoff.

#### 6.2.2.1 Acid Rain Mobilisation.

Acidic waters can dissolve inorganic compounds and therefore release solid associated metal forms into the dissolved phase. Metal species

which are attached to the solid surface can also be released to the dissolved phase because of hydrogen ion saturation of surface sites.

The acidity of the rainfall reaching the road surface during the study period was in the pH range 3.8-4.9. Prevailing wind and local atmospheric conditions are critical for rainfall acidity in the Gothenburg area. Lower pH values are associated with south-westerly winds and the higher, relatively neutral pH rainfall occurs in connection with northerly winds. The initial acid rain dissolution of road dust associated metals should increase with decreasing pH.

The total mass balance for Cd in storm 6B shows that 52% (1.58 mg) of the Cd available for removal from the road surface and the incoming atmospheric fallout is washed off in road runoff. There are two possible explanations for this observation:

- a) Cadmium is enriched in certain easily mobilised road dust fractions. This physical mobilisation process can be supported by the 1.5 mg Cd that was found in the <125  $\mu\text{m}$  fraction of road solids (out of a total of 2.71 mg Cd).
- b) Road dust associated Cd is chemically transferred to the dissolved phase by acidic incoming rainfall, followed by direct washoff.

The physical mobilisation process would require the mobilisation of 5.4 Kg of road dust to provide 1.5 mg Cd from the direct physical mobilisation of the <125  $\mu\text{m}$  fraction. However, only 0.16 Kg of road dust was washed off in the road runoff of storm 6B. Even taking the finer metal enriched fractions (<63  $\mu\text{m}$ ) of road dusts into account, 2.3 Kg of road dusts must be mobilised to account for 0.6 mg of Cd and therefore this process can be considered to be relatively unimportant. However, a chemical solubilisation process does provide a possible explanation. Analysis of road dust particles finer than 1000  $\mu\text{m}$  shows that they provide a readily released source of Exchangeable Cd (Figure 6.1) which can be dissolved and washed off by the acidic rainfall.

ROAD DUST  
HEAVY METAL SPECIATION  
17TH JULY 1984 CADMIUM

▨ EXCHANG.  
▩ ORGANIC

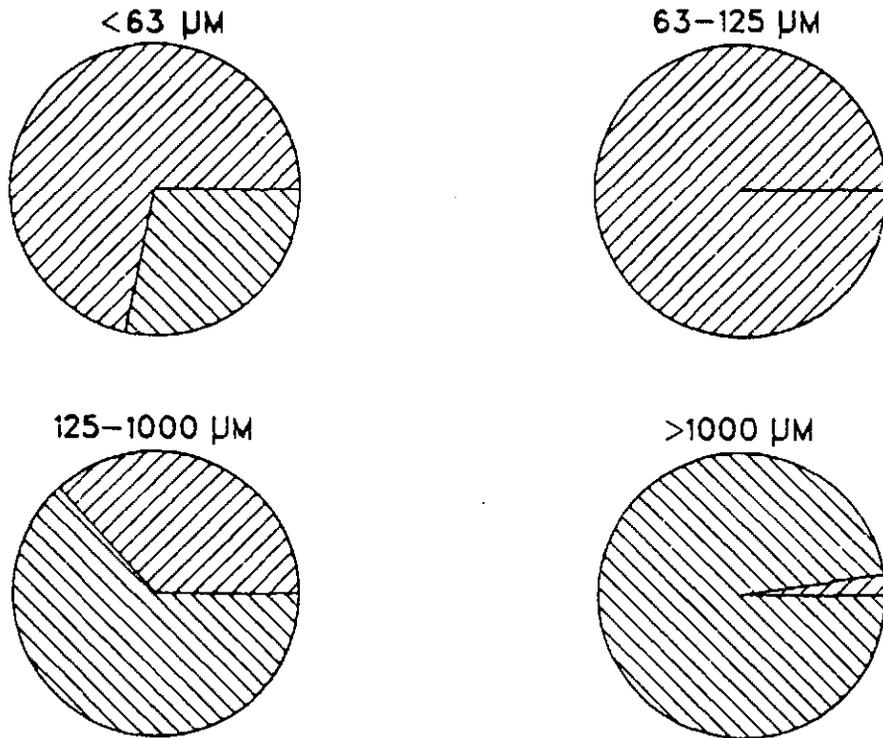


Figure 6.1 Cadmium Speciation in Size Fractionated Road Dusts.

Exchangeable metal released by the solubilisation process can account for all the Cd and Cu in road runoff. However, only between 15.4% and 40.3% of Pb is released from the Exchangeable fraction to road runoff. Lead may be more strongly sediment associated in the Exchangeable fraction than either Cd or Cu and therefore the prolonged acid rain washing of storm GB was required to release 40.3% of the available Pb.

Most of the dissolved metal released from road dusts is present in the road runoff as Chelex Removeable species. Therefore, during the transfer of metal from the Exchangeable road dust fraction to the

dissolved phase it remains as relatively free and weakly complexed inorganic/organic species.

As a great proportion of the Exchangeable road dust fraction is washed off, certainly for Cd, Cu and Zn, the accumulation of metals in road dusts during dry periods may determine the extent of acid rain mobilisation. Road dust and associated metal was found to continually accumulate on the road surface. Road dust accumulated at a rate of 0.9 g/m<sup>2</sup>/day, giving a rate for the overall catchment of 351 g/day. A gullypot outflow washoff range of 28.2-467.1 g was found for five of the 17 storms in the 68 day study period.

The rate of metal accumulation on the catchment is shown in Table 6.4.

Table 6.4 Road Surface Dust Metal Accumulation and Removal Rates.

	Road Dust Metal Accumulation mg/day	Average Available Metal/Storm Event mg	Gullypot Outflow Total Metal Removal Rate Range mg/Storm Event
Zinc	53.5	214	135-477.5
Cadmium	0.062	0.25	0.91-3.63
Lead	56.2	224.8	75.7-891.8
Copper	18.7	74.8	31.8-193.9

The total metal accumulation rate can be converted into the average available metal per storm event, the average dry period being four days, and this can be compared with the gullypot metal outflow range for five storm events. The average available metal values for Zn, Pb and Cu fall within the outflow range. This suggests that these metals are washed off the road surface and through the gullypot, either at

the end of the dry period or after short term storage in the gullypot. More Cd was washed through the gullypot system than accumulated in road dusts, the excess might be accounted for by atmospheric fallout during the storm event. The acid rain solubilisation process therefore greatly increases the rate of metal removal from accumulated road dusts.

#### 6.2.2.2 Chemical Sorting of Metal Species.

When road dusts are physically mobilised by rainfall there may be changes in the metal species distribution due to chemical interactions.

This is clearly exhibited by a comparison of the gullypot mass balances for sedimentary Pb fractions during storm 6B. 24% of Exchangeable Pb (187.6 mg), 5.4% of Carbonate and Hydrous Metal Oxide Pb (56.1 mg) and 1.4% of Organic Pb (9.5 mg) are present in the solids of road runoff compared to the original road dusts. Clearly there is a preferential sorting of the more weakly associated metal fractions.

An analysis of road dust speciation for Pb (Figure 6.2) shows that the Carbonate and Hydrous Metal Oxide fraction is present in significant amounts in the smaller size fractions and therefore preferential washoff alone cannot explain the enrichment of Exchangeable Pb in road runoff solids. Clearly chemical changes are creating a transfer of Pb amongst the fractions, both solid and liquid, giving an enrichment in the Exchangeable fraction.

Chemical sorting was also observed for Zn and Cu with similar enrichments in the more weakly associated fractions. However, this was not observed for Cd as acid rain solubilisation was very effective at reducing solid associated Cd loadings in road runoff. One explanation for the chemical sorting of road dust metal fractions may be changes in pH which cause the adsorption/desorption of dissolved metal species to solid surfaces.

ROAD DUST  
HEAVY METAL SPECIATION  
17TH JULY 1984 LEAD

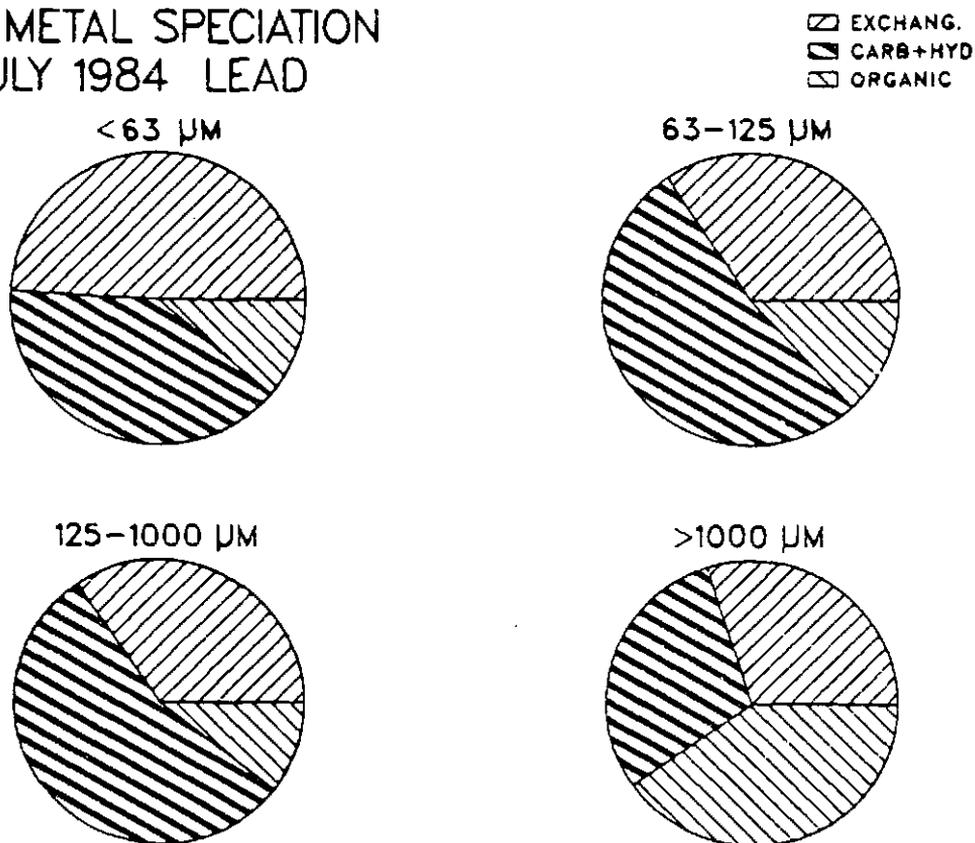


Figure 6.2 Lead Speciation in Size Fractionated Road Dusts.

6.2.3 Free and Weakly Complexed Metal Ion Reaction.

When acidic rainfall reaches the road surface it is initially weakly buffered by road dust derived organic and inorganic salts. On entry to the gullypot the road runoff undergoes further buffering by the gullypot liquor which therefore initially remains at the pH established between storms (normally  $\text{pH} \approx 7.0$ ). Subsequently the incoming road runoff reduces the pH to between 4.0 and 5.0. However, as a result of the weak buffering at the beginning of storm events a Buffer Time Zone is established where no drop in gullypot pH occurs, despite incoming road runoff (Table 6.5).

Table 6.5 Free and Weakly Complexed Metal Reaction during the Buffer Time Zone of different Storm Events.

Storm Code	Buffer Time Zone*	Reactive Free and Weakly Complexed Metal
6A	07.32-07.38	Cd, Pb, Cu
6B	09.09-09.24	Cd, Pb, (Zn), (Cu)
6C	08.42-08.53	Cd, Pb
6E	10.43-10.46	Cd, Pb, (Cu)
6F	12.00-12.07	Cu

(Metal) = weak reaction

\*Measured in the gullypot

At the same time as hydrogen ions are buffered a similar reaction occurs for certain metals (Table 6.5) with a reduction of free and weakly complexed metal ions, i.e. increase of  $pM_{\text{Electrochemically Available}}$  ( $pM_{\text{E.A.}}$ ). A clear example of this is seen for  $pPb_{\text{E.A.}}$  in the gullypot during storm 6B (Figure 6.3). During the Buffer Time Zone  $pPb_{\text{E.A.}}$  remains high, despite a high total dissolved Pb concentration of up to 95  $\mu\text{g/l}$ . In the gullypot  $pPb_{\text{E.A.}}$  lags slightly after the initial rapid decrease of pH by some 12 minutes creating a longer Metal Reaction Time Zone. This extension may be attributed to dissolved organic compounds, enriched in the stirred up gullypot, which inhibit the release of Electrochemically Available Pb. A further increase of  $pPb_{\text{E.A.}}$  later in the storm is related to the dilution-exhaustion of dissolved Pb, rather than complexation.

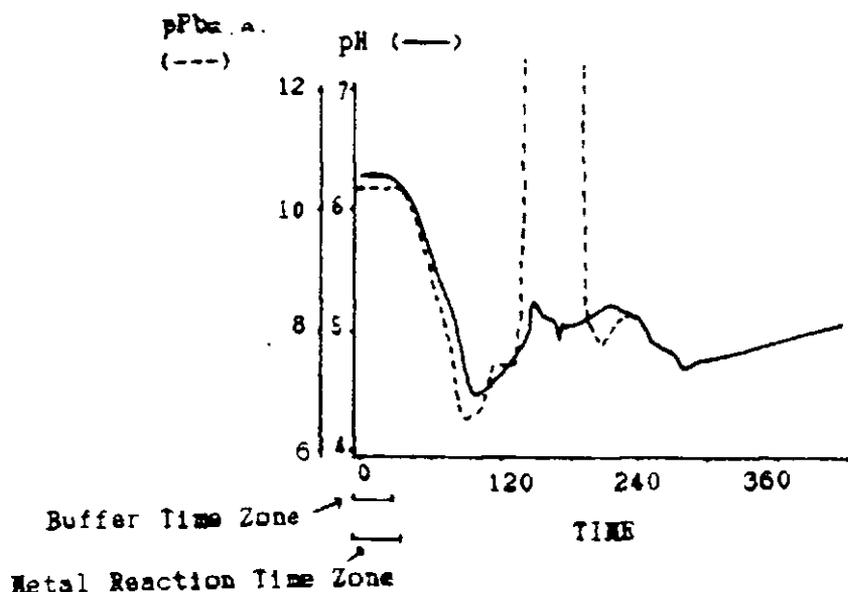


Figure 6.3 pPb<sub>e,a.</sub> Variations as influenced by the Buffer Time Zone. Time in Minutes

The initial gullypot sample of storm 6B had only 0.01% in an Electrochemically Available form, out of a dissolved Pb concentration of 92.3 µg/l. Yet, for the same storm, 67% of Pb in atmospheric fallout was in an Electrochemically Available form out of a dissolved Pb concentration of 13.1 µg/l. In terms of loadings this reduction of Electrochemically Available metal between atmospheric fallout and gullypot outflow is not always significant (Table 6.6), although, in some cases, it may be up to 60%. This is complicated by the solubilisation of metals through the gullypot system giving rise to an increase of free and weakly complexed metal. In addition, only the first part of the storm event is affected by the Metal Reaction Time Zone. However, the extent of Electrochemically Available metal reduction may further increase within the in-pipe system where more buffering and more sediment mobilisation may occur.

Table 6.6 Reduction of Electrochemically Available Metal in the Gullypot System.

Storm code	% Reduction of Electrochemically Available Metal between Atmospheric Fallout and Gullypot Outflow			
	Zinc	Cadmium	Lead	Copper
6B	27.7	id	38.2	(0.8)
6C	(28.2)	id	id	(66.9)
6D	id	40.8	(31.7)	id
6E	7.1	id	13.5	11.6
6F	19.7	58.4	10	59.2

id = insufficient data

(%) = increase

#### 6.2.4 pH/Surface Area Dependent Suspended Solid Metal Transport.

Surface area dependent uptake may be an important transport mechanism for metals through the gullypot system. This is particularly relevant for fine sediment as the surface area of spherical particles increases exponentially with decreasing particle diameter. As the surface is a focus of important reactions involving metals (see Section 2.7.2) small particles might be expected to exert a much greater metal reaction activity per unit weight than large particles.

It has been found that at low suspended solid concentrations, which are usually associated with low flow conditions, small particles containing elevated metal levels are preferentially washed off the urban surface. During higher flows lower suspended solid metal concentrations are found, but the presence of larger particles is also observed (Harrison and Wilson 1983).

Two concepts may be put forward to explain the above finding:

a) Harrison and Wilson (1983) proposed that the hydrodynamic sorting of highway dust might explain these results.

b) Surface area dependent uptake scavenges metals from the dissolved phase onto reactive surfaces such as organic complexing sites or hydrous Fe and Mn oxides. The greatest metal enrichment would be expected in the finest solids which have the greatest unit surface area.

A combination of these two concepts is presented in Figure 6.4. In this theoretical situation road dust size sorting is the dominant control on metal concentration above 50 mg/l suspended solids. However, during low flow conditions with fine high surface area particles, i.e. below 50 mg/l suspended solids, surface area dependent uptake becomes important. The change over point for the surface area dependent uptake process is the intercept,  $M_i$ , expressed in mg/l suspended solids. When  $M_i$  is zero sediment metal concentrations can only be ascribed to the hydrodynamic sorting of road dusts. As  $M_i$  increases so too does the extent of surface area dependent uptake. The value of  $M_i$  can therefore be related to the extent of enrichment of metals in suspended solids over road surface dusts.

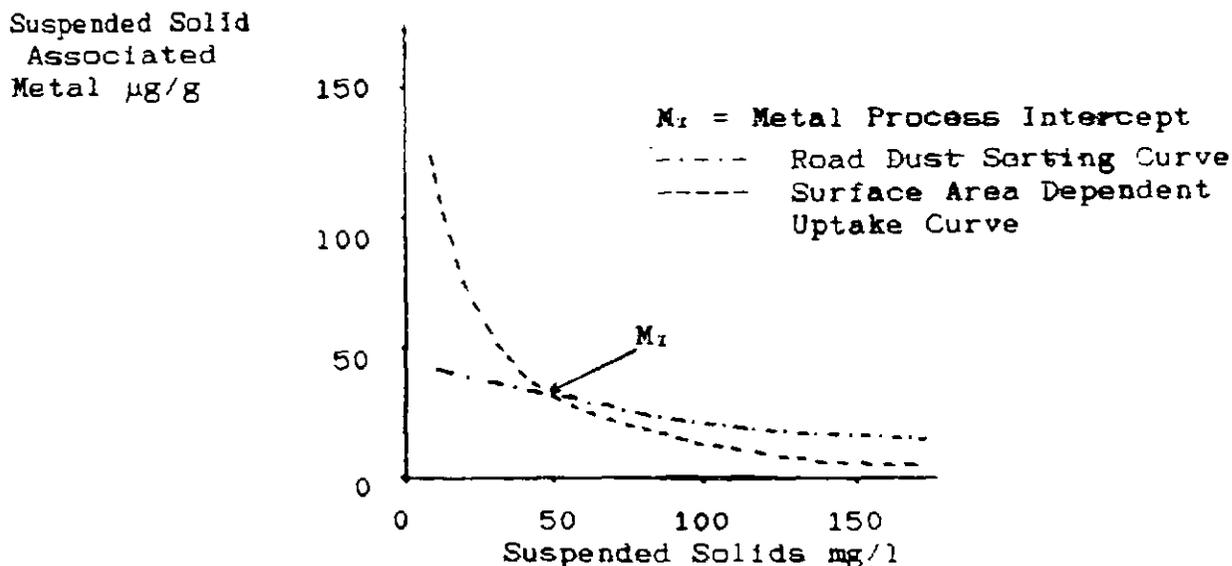


Figure 6.4 Conceptual Representation of Processes affecting Metal Concentration at different Suspended Solids Concentrations.

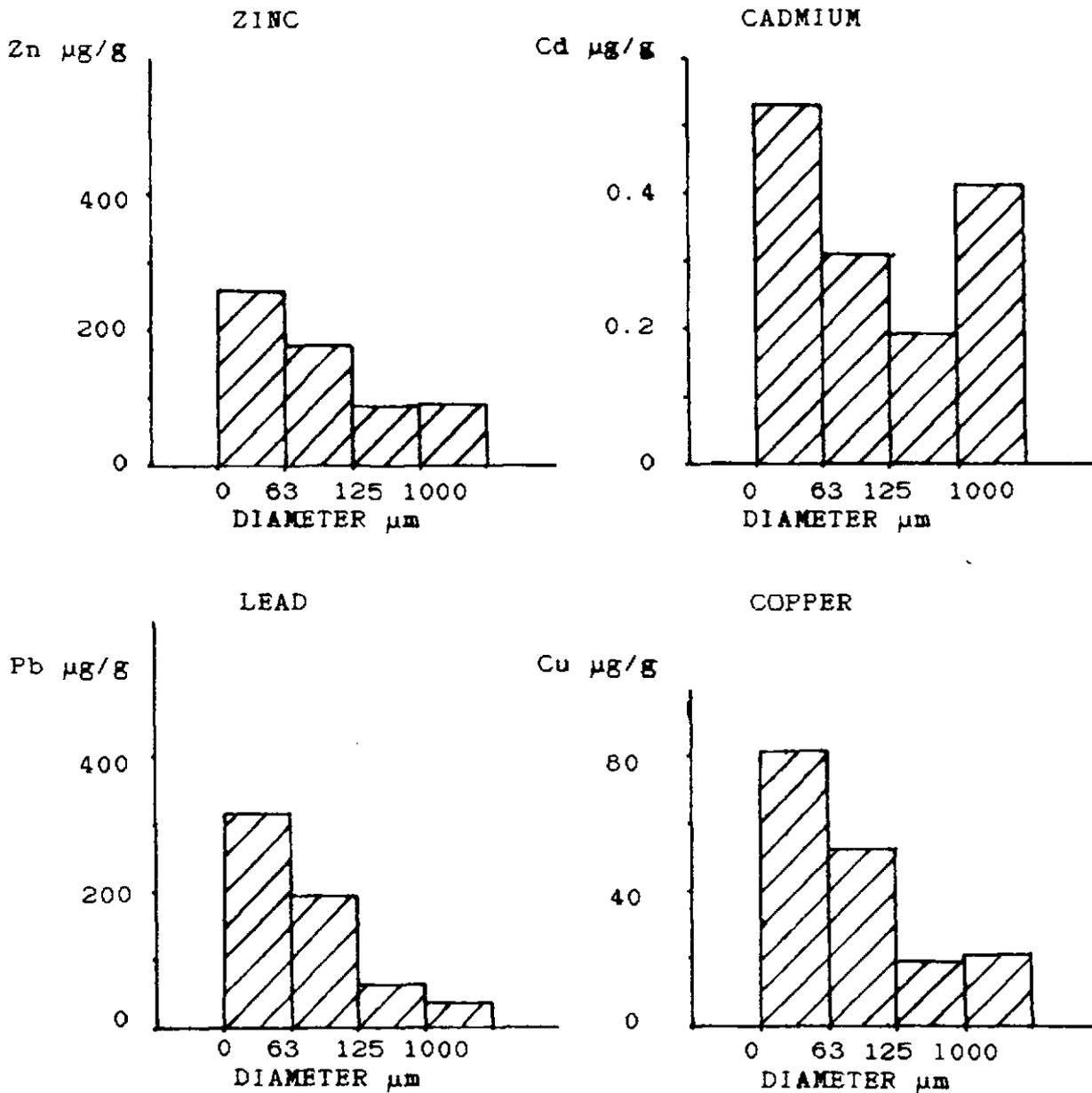


Figure 6.5 Metal Size Distribution on the Chalmers Parking Lot, 17.07.84.

The conceptual curve for road dust sorting (Figure 6.4) was obtained from the general trend of metal concentrations in size fractionated road dusts on the Chalmers catchment (Figure 6.5). Metal concentrations clearly increase with decreasing particle size. Based on the work of Ellis and Harrop (1984) only 5% of solids discharged to

gullypots are less than 60  $\mu\text{m}$  (66% is 400-3000  $\mu\text{m}$ ), although during low flow conditions more fine solids may be present. The finest road dust metal concentration (<63  $\mu\text{m}$ ) may therefore give an indication of the highest metal concentration values expected on the road dust sorting curve. Therefore if surface area dependent metal uptake is occurring through the gullypot system then an increase of suspended sediment metal concentration over fine metal dust concentration would be expected. A typical example of this type of metal enrichment is shown for Pb in Figure 6.6. Not only are road runoff solids metal enriched over road dust fines, but therefore also further enriched in the gullypot and gullypot outflow. The enrichment is by up to a factor of 10 in road runoff compared to road dusts. This suggests that surface area dependent metal uptake may be a continuous process through the gullypot system.

As both road runoff and gullypot waters are increasingly buffered with respect to rainfall it can be argued that this pH gradient may increase, or even be the prime cause of, surface area dependent metal uptake. The proposed mechanism for metal transport would envisage that during acidic rainfall events certain metal species are solubilised from road surface dusts, as described in Section 6.2.2.1. Buffering of the acidity by road salts in the road surface water microlayer would cause the hydrodynamically sorted fines to take up free and certain weakly complexed metal ion species. The amount of metal uptake will depend on the nature of the solids, the amount of metal available and the degree of buffering, as well as prevailing hydrodynamic conditions.

The greatest metal uptake would be expected in low intensity, long rainfall events (Table 6.7). This is because during light showers fine particles only are mobilised and the runoff waters remain buffered for a longer time period. This results in a higher average metal concentration, particularly for Cd and Pb, in a light rainfall than in a thunderstorm. However, even in a heavy thunderstorm such as storm 6E, metal concentrations are well above the less than 63  $\mu\text{m}$  fraction of road dusts, particularly for Cd, Pb and Cu.



mobilised early in the storm event which, perhaps in a misleading way, extrapolates the surface area dependent uptake curve to high concentrations, but makes no difference to the  $M_r$  values.

Table 6.7 Average Sediment Metal Concentrations in Gullypot Outflow and Fine Road Dusts.

	Average Sediment Metal Concentration $\mu\text{g/g}$		
	Gullypot Outflow		Road Dusts $<63 \mu\text{m}$
	Storm 6C (2.9 mm/8.7 hours)	Storm 6E (9.7 mm/1 hour)	03.08.84
Zinc	417.1	354.5	234.3
Cadmium	12.4	4.6	0.35
Lead	2092.0	1279.9	358.8
Copper	329.0	234.9	78.2

Cadmium has an elevated  $M_r$  value in the gullypot which is reflected in the gullypot outflow and it can therefore be suggested that surface area dependent metal uptake may be important for Cd in the gullypot. If the process continued in the below ground system then pH/surface area dependent metal uptake may become the dominant transport mechanism. In the case of Cu the  $M_r$  value in the gullypot outflow reflects incoming road runoff, with only a minor apparent effect from the high  $M_r$  value in the gullypot.

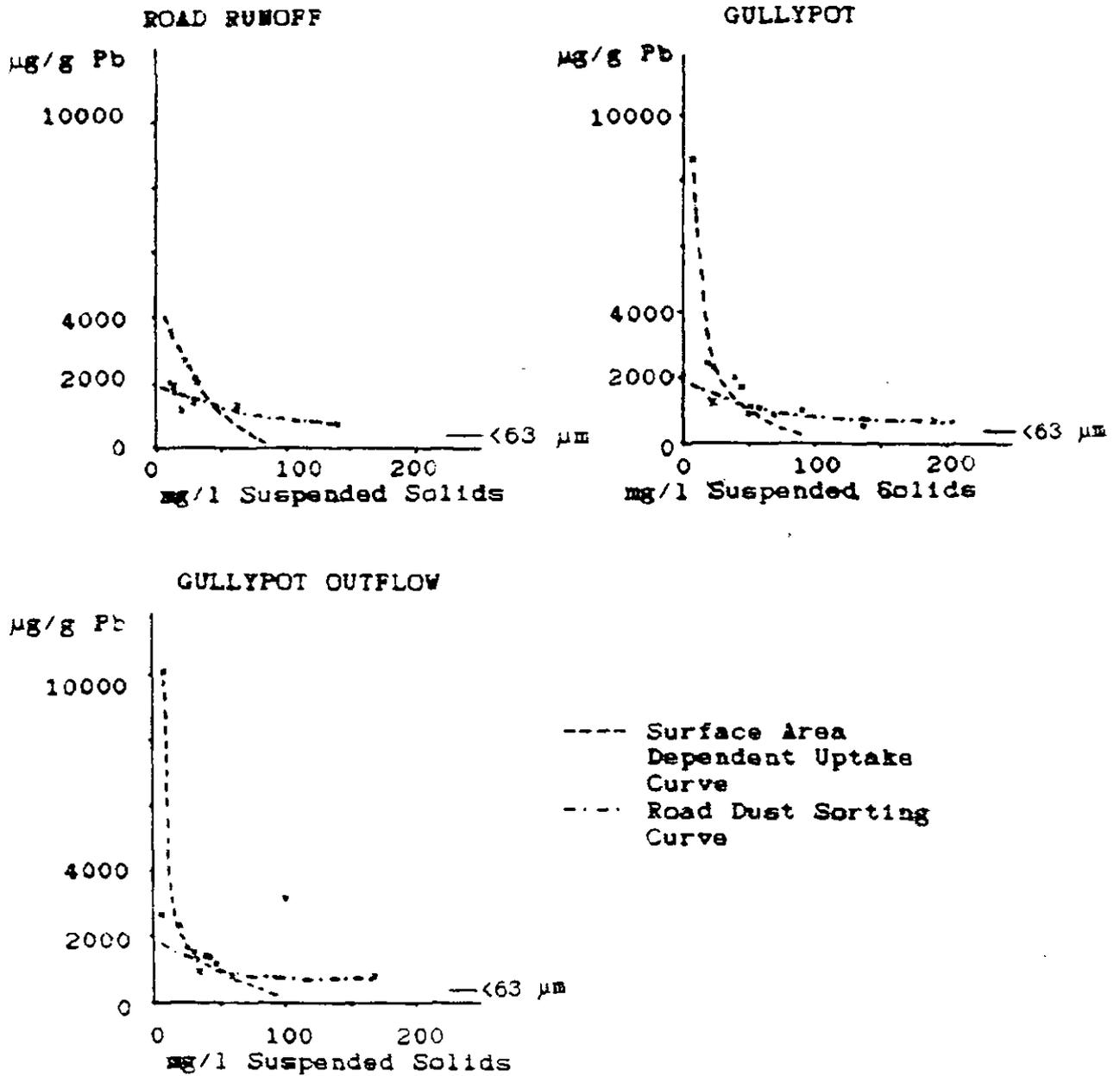


Figure 6.7 Relationship of Suspended Solid Lead Concentration against Suspended Solids, for Road Runoff, Gullypot and Gullypot Outflow.

Table 6.8  $M_1$  Values for Metals in Road Runoff, Gullypot and Gullypot Outflow.

$M_1$ Values, mg/l Suspended Solids (Storm 6B)			
	Road Runoff	Gullypot	Gullypot Outflow
Zinc	nr	40	40
Cadmium	22	43	38
Lead	44	48	44
Copper	36	57	39

nr = no relationship

Although pH may be the most important parameter affecting surface area dependent metal uptake, it is recognised that other parameters may increase or decrease suspended solid metal adsorption processes. Particulate organic carbon and hydrous Fe and Mn oxides may increase metal adsorption and these have been fractionated using the speciation scheme described in Chapter 4. A decrease of redox potential or an increase of ionic strength may reduce metal adsorption.

The individual components, such as organics and hydrous metal oxides, in the washoff solids may exert different uptake constants and capacities. The activity of the surface will also depend on the metal species being adsorbed. Table 6.9 shows the metal fractions which exhibit a pH/surface area dependent metal uptake at different stages in the gullypot system.

Those metal fractions which show a weak relationship, or none at all, with suspended solids are usually not enriched over the same metal fraction in the less than 63  $\mu\text{m}$  size fraction of road dusts. This means that the  $M_1$  value is at or close to zero.

Table 6.9 Surface Area Dependent Metal Uptake for different Metal Fractions.

		Exchangeable Fraction	Carbonate and Hydrous Metal Oxide Fraction	Organic Fraction
Zinc	Road Runoff	-	(+)	(+)
	Gullypot	+	(+)	(+)
	Gullypot Outflow	(+)	+	+
Cadmium	Road Runoff	+	nd	+
	Gullypot	+	nd	+
	Gullypot Outflow	+	nd	+
Lead	Road Runoff	+	+	(+)
	Gullypot	+	+	(+)
	Gullypot	+	+	-
Copper	Road Runoff	+	(+)	(+)
	Gullypot	+	(+)	(+)
	Gullypot Outflow	(+)	(+)	(+)

+ = significant relationship  
 (+) = weak relationship  
 - = no relationship  
 nd = not detected

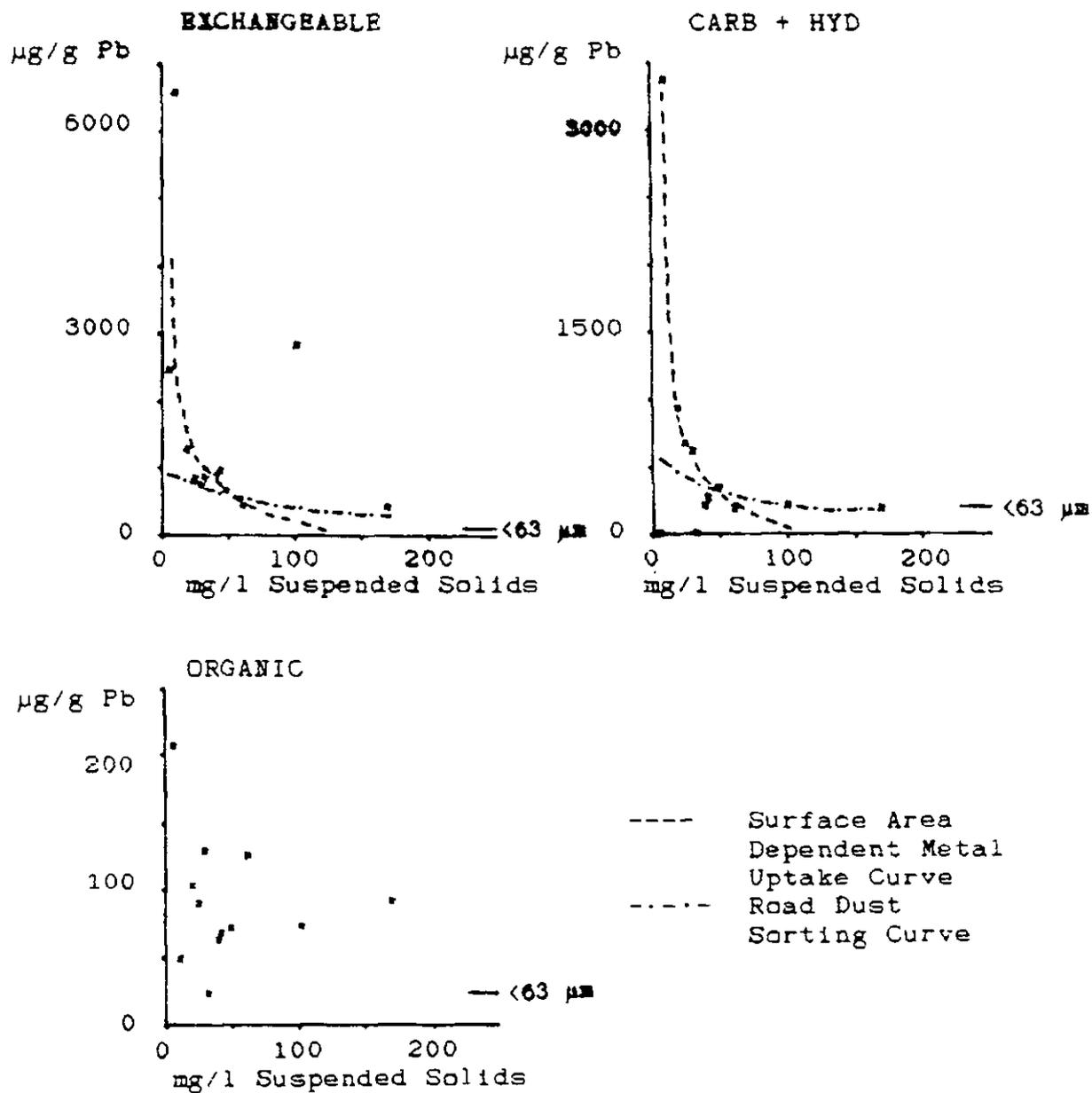


Figure 6.8 Relationship of Suspended Solid Lead Fractions with Suspended Solids for Gullypot Outflow, Storm 6B.

The fractions which show a significant relationship have higher metal concentrations than the less than 63 μm fraction of road dusts. As can be seen in Figure 6.8, for Pb fractions in the gullypot outflow of

storm 6B, the Exchangeable fraction has a higher  $M_1$  value (54 mg/l suspended solids) than the Carbonate and Hydrous Metal Oxide fraction (51 mg/l suspended solids) as well as a greater metal enrichment over the same fractions in fine road dust. The Exchangeable fraction therefore provides more competitive sites for Pb species uptake than the Carbonate and Hydrous Metal Oxide fraction. The Organic fraction cannot be ascribed a  $M_1$  value as was anticipated from Table 6.9. However, although not significant in terms of total adsorbed Pb, some Organic fraction values are higher than expected from fine road dust concentrations. These deviations may be attributed to certain strongly binding organic ligands which are selective for Pb and may not be present in all the washed out solids. It is clear from Table 6.9 that the Exchangeable fraction most frequently shows a significant relationship which tends to confirm that the solid surface is actively involved in metal uptake. Lead and Cd show the most consistent uptake at different stages of the gullypot system, while the uptake of Zn and Cd may depend on the physical and chemical characteristics of the solids present during transport.

Table 6.10 shows the  $M_1$  values obtained for the different metal fractions in storm 6B. Zinc shows no pH/surface area dependent uptake in the road runoff. Usually Zn concentrations are similar to the less than 63  $\mu\text{m}$  fraction of road dusts and therefore the Zn concentrations in sediments leaving the road surface may simply reflect hydrodynamic sorting. However, uptake of Zn may be occurring into the Carbonate and Hydrous Metal Oxide and Organic fractions in the gullypot. These processes are also reflected by similar  $M_1$  values for the gullypot outflow. In terms of higher concentrations and a higher  $M_1$  value the surface area uptake of Zn is greatest into the Carbonate and Hydrous Metal Oxide fraction.

Table 6.10  $M_r$  Values for Metal Species, Storm 6B.

		$M_r$ Values (mg/l Suspended Solids)		
		Exchangeable Fraction	Carbonate and Hydrous Metal Oxide Fraction	Organic Fraction
Zinc	Road runoff	nr	nr	nr
	Gullypot	nr	37	23
	Gullypot outflow	nr	37	25
Cadmium	Road runoff	49	nr	39
	Gullypot	55	nr	43
	Gullypot outflow	30	nr	45
Lead	Road runoff	53	37	nr
	Gullypot	71	47	nr
	Gullypot outflow	54	51	nr
Copper	Road runoff	nr	42	nr
	Gullypot	66	nr	32
	Gullypot outflow	nr	41	30

nr = no relationship

Cadmium and Pb show the most significant concentration enrichments in road runoff over fine source road dusts. Cadmium shows uptake into the Exchangeable and Organic fractions (Table 6.10). Road runoff has a high  $M_r$  value for Exchangeable Cd, with no apparent effect on the gullypot outflow by the higher  $M_r$  value in the gullypot. Therefore

most of the uptake into the Exchangeable Cd fraction occurs on the road surface. Organic Cd has an increased  $M_1$  value in the gullypot in addition to the already high road runoff value. This indicates that surface area dependent Cd uptake occurs into the Exchangeable and Organic fractions on the road surface, with further Cd enrichment in the Organic fraction in the gullypot.

Lead demonstrates significant  $M_1$  values for the Exchangeable and Carbonate and Hydrous Metal Oxide fractions, with the greatest concentration enrichment in the Exchangeable fraction (Table 6.10). Although the gullypot has the highest Exchangeable Pb  $M_1$  value (71 mg/l suspended solids) the gullypot outflow  $M_1$  value is dominated by incoming road runoff. However, the gullypot does seem to give rise to an increased  $M_1$  value for the Carbonate and Hydrous Metal Oxide fraction. This could be related to the oxidation of gullypot waters allowing the adsorption of metals onto freshly formed hydrous metal oxide surfaces. Such processes increase in the more oxidising gullypot outflow, giving rise to a steadily increasing  $M_1$  value. This may be an indication of redox/surface area dependent metal uptake.

Copper shows a significant metal enrichment in the gullypot for the Exchangeable fraction, but there is no observable effect in the gullypot outflow (Table 6.10). However, the gullypot outflow is influenced by a slight enrichment effect for the Organic fraction in the gullypot whereas for the Carbonate and Hydrous Metal Oxide fraction road runoff appears to be the controlling factor. However, in general the enrichments are relatively small and therefore, in the same way as Zn, hydrodynamic sorting tends to dominate the gullypot outflow suspended sediment concentrations for Cu.

#### 6.2.5 Metal Increase in the Gullypot Liquor between Storm Events.

Between storm events the gullypot sediment and liquor might be expected to undergo changes in composition as a result of biological and chemical reactions.

a) Bacterial activity can give rise to sediment maturation and the release into the water column of maturation products. Some evidence for this can be obtained from parameters measured in the gullypot liquor (Figure 6.9). Dissolved oxygen decreases to 60-80% saturation after a storm event and then remains relatively constant over the dry period. Clearly there is a balance maintained between sedimentary oxygen consumption and diffusion into the gullypot liquor from the atmosphere. When the gullypot sediment is mobilised during a storm event redox potential and dissolved oxygen concentrations decrease and ATP concentration increases (from 0.7 up to 4.5  $\mu\text{g ATP/l}$  during storm 6E) which may indicate bacterial activity.

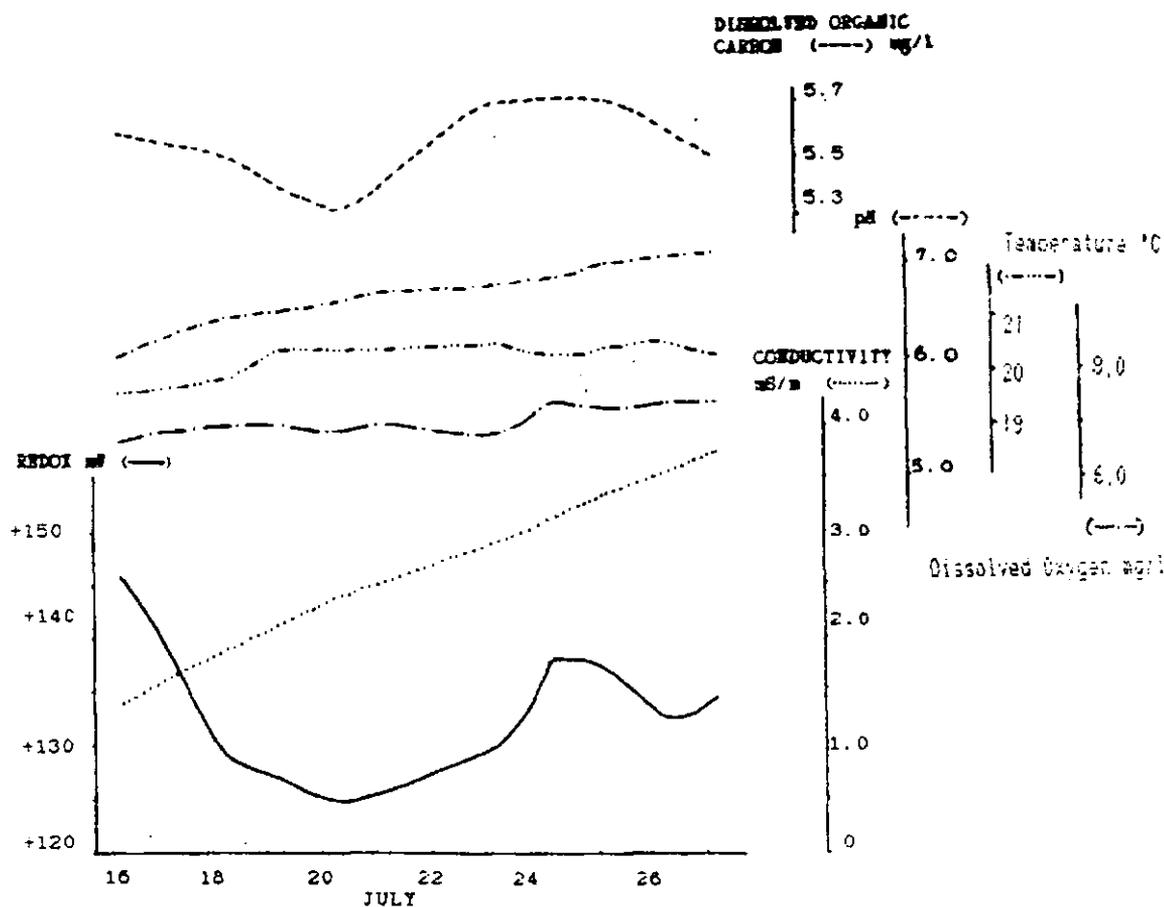


Figure 6.9 Variation of Controlling Parameters during a Dry Period in the Gullypot.

b) Chemical reactions occur in the acidic liquor and sediment. Both conductivity and pH increase gradually over the dry period (Figure 6.9), with pH increasing rapidly for a few hours after each storm event. Dissolved Ca also increases gradually during the dry period, from 1.4 to 10.6 mg/l. These increases may be related to the corrosion of the cement gullypot structure releasing Ca and bicarbonate, resulting in increases of conductivity and pH. Redox, dissolved oxygen and temperature did not show any distinct changes in the gullypot liquor over the dry period.

These biological and chemical reactions have an interesting effect on metal species. After a storm event the gullypot liquor is relatively clean and it overlies a metal rich sediment. Sediment maturation and acidic dissolution may release metals into the gullypot liquor.

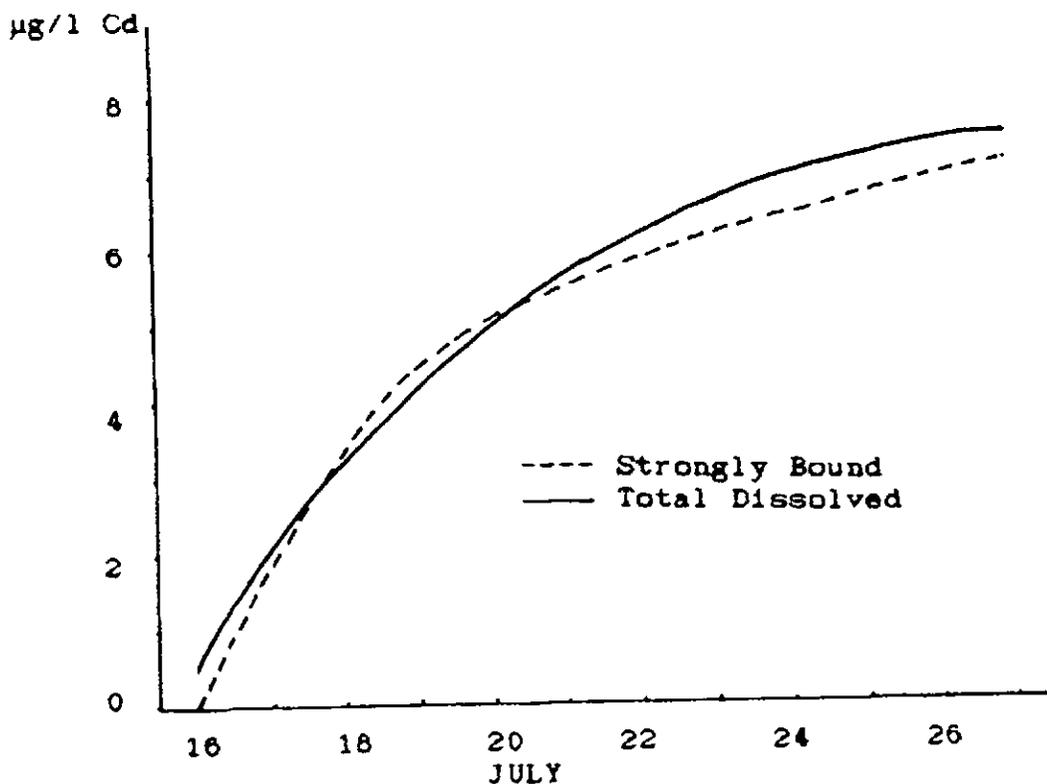


Figure 6.10 Dissolved Cd Increase in the Gullypot during a Dry Period.

In general the dissolved metal concentrations increase in the gullypot liquor between storms, although the pattern of increase is often rather irregular. This is not the case for total dissolved Cd and the Strongly Bound soluble fraction which increase over a period of 11 dry days as shown in Figure 6.10. The affinity of dissolved Cd for the Strongly Bound fraction suggests that it may be that the Cd is bound by organic compounds released by bacterial action on the sediment.

The curves show a relatively rapid release of dissolved Cd during the first few days and appear to be tailing off towards equilibrium. The time to reach half maximum concentration would give a characteristic parameter for the release of Cd under the redox, pH and Cd concentration conditions of the gullypot sediment which was present in the gullypot. As the curve in Figure 6.10 is asymptotic it is difficult to determine the time of maximum Cd concentration with any precision. However, as the total dissolved Cd curve is of a similar type to that of Michaelis-Menton for enzyme kinetics, equation 6.1 may be applied.

$$[Cd]_{Diss} = \frac{Max[Cd]_{Diss} \times time}{t_{1/2} + time} \quad 6.1$$

where  $t_{1/2}$  = time to reach half maximum Cd concentration  
time = time for  $Max[Cd]_{Diss}$

A double reciprocal plot gives a straight line, according to equation 6.2, where the slope is  $t_{1/2}/Max[Cd]$ , the y-axis intercept is  $1/Max[Cd]$  and the negative x-axis intercept is  $-1/t_{1/2}$ .

$$\frac{1}{[Cd]_{Diss}} = (t_{1/2} / Max[Cd] \times time) + \frac{1}{Max[Cd]_{Diss}} \quad 6.2$$

The data points from Figure 6.10 were therefore re-plotted, according to equation 6.2, to give Figure 6.11. This gives a value for  $t_{1/2}$  of 76.9 hours and  $Max[Cd]_{Diss}$  of 9.7  $\mu\text{g/l}$ . These values can then be used in equation 6.1 to calculate the dissolved Cd concentration at any time during the dry period.

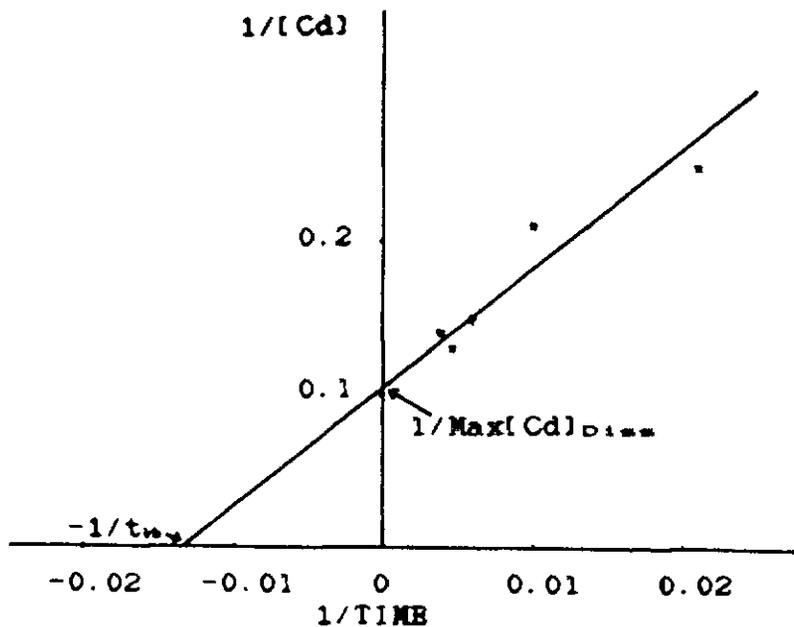


Figure 6.11 Double Reciprocal Plot Allowing Precise Determination of  $t_{1/2}$  and  $\text{Max}[Cd]_{\infty}$

However, the pattern of dissolved metal increase is complicated by the presence of suspended solids and a gradually increasing pH (Figure 6.9) and similar relationships are not found for Cu, Pb and Zn. pH controlled adsorption to solids may explain the slight fall-off in dissolved Cd levels after 11 days (Figure 6.10) which has also been observed for Pb. Copper and Zn show fluctuating dissolved concentrations because the steadily increasing pH causes an increasing tendency for metal adsorption to suspended solids (Figure 6.12). Therefore the dissolved metals released from the gullypot sediment may be scavenged by gullypot liquor suspended solids when the pH has increased enough to cause surface adsorption.

For all four metals, total metal concentrations in the gullypot increase in accordance with equation 6.1 over the dry period. Table

6.11 gives the  $t_m$  and Max[metal] values for two different dry periods for total metal.

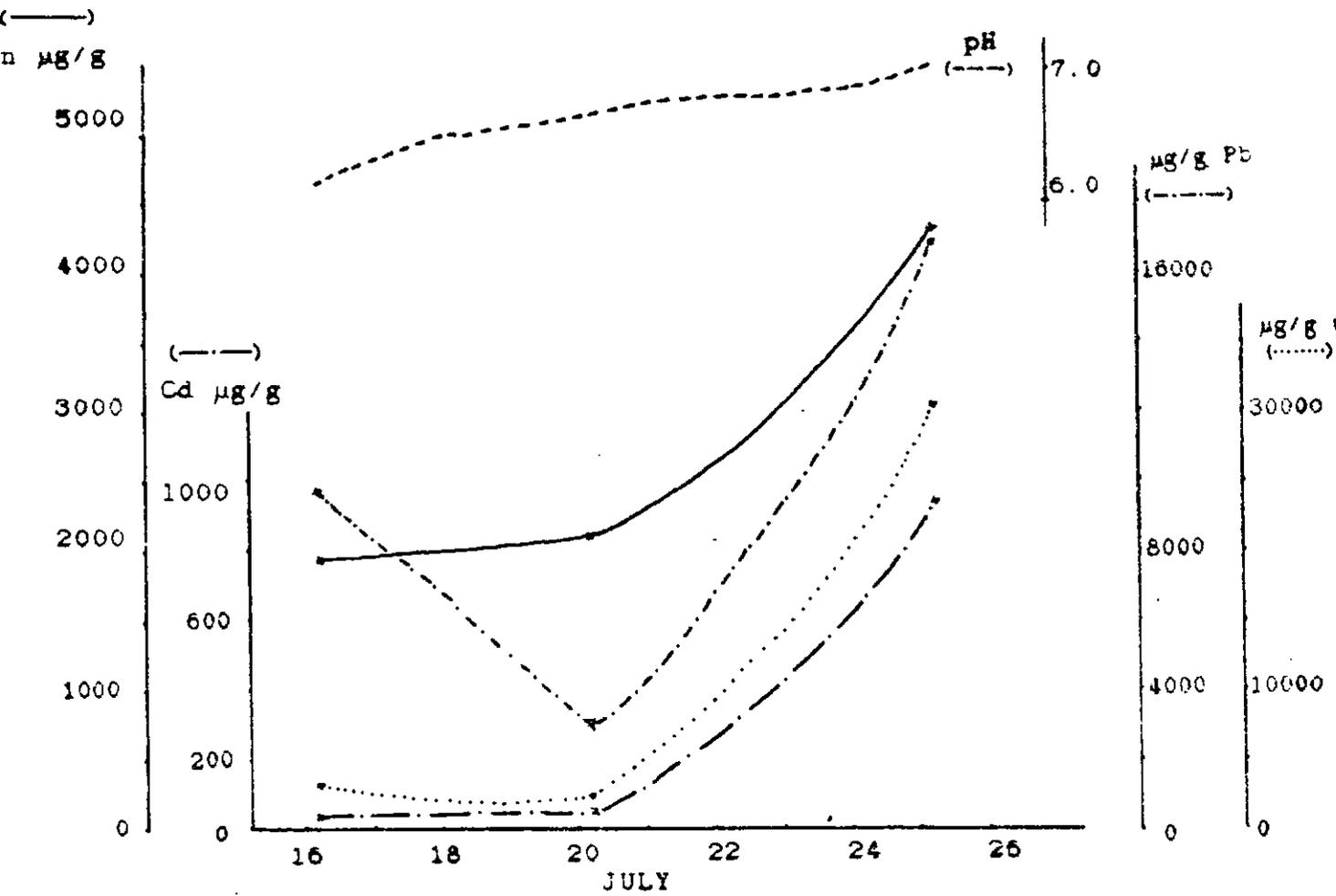


Figure 6.12 Variations of Suspended Solid Metal Concentrations between Storm Events.

Table 6.11 Values of  $t_{1/2}$  and Max[metall] for Metals in the Gullypot Liquor during Dry Periods.

Dry Period	Metal	$t_{1/2}$ (hours)	Max[metall] $\mu\text{g/l}$
16.07 to 28.07	Zinc	55.6	406.5
	Cadmium	117.6	13.0
	Lead	122.0	192.3
	Copper	61.0	454.5
06.08 to 15.08	Zinc	1.2	79.4
	Cadmium	66.7	4.0
	Lead	27.8	120.5
	Copper	11.8	277.8

The first dry period, 16.07.84 to 28.07.84, was preceded by three small rainfall events (0.1 mm, 2 mm and 0.1 mm) over the preceding three days. Mass balances show that these types of low volume rainfall events cause a net accumulation of gullypot sediment metals. In contrast the second dry period, 06.08.84 to 15.08.84, occurred after three days of heavy rainfall (9.5 mm, 4.6 mm and 11.6 mm). In terms of heavy metal mass balances large rainfall events cause a net reduction of sedimentary metals due to physical mobilisation. The antecedent rainfall conditions are therefore important in deciding the amount of metal available in the gullypot sediment.

The first dry period had a greater amount of sedimentary metal available and this led to greater  $t_{1/2}$  and Max[metall] values than was found for the second dry period. The amount of metal in the gullypot liquor therefore depends on:

- a) The initial gullypot liquor metal concentration.
- b) The initial sedimentary metal concentration.

c) The length of dry period until Max{metal} is reached.

The shortest  $t_w$  times, but highest maximum concentrations were found for Zn and Cu. This may be the result of Zn and Cu, bound to the surface of basal sediment, being released to the gullypot liquor by acid dissolution. Cadmium and Pb were released more slowly which suggests that these metals are primarily released into the gullypot liquor, with organic maturation products, by bacterial activity on the gullypot sediment.

#### 6.2.6 Contribution of Gullypot Liquor and Sediment to Metals in the Gullypot Outflow.

The interstitial sedimentary water of gullypots appears to be an important highly enriched source of heavy metals. A significantly high concentration of all four metals, particularly associated with the Strongly Bound fraction, occurred when the gullypot contents were disturbed by a small storm. Additionally significant increases of dissolved organic carbon and suspended solids were observed (Table 6.12).

Table 6.12 Heavy Metals and Controlling Parameter Concentrations in the Gullypot after Small Storm Events.

Preceding Storm	Storm Volume (litres)	Dissolved Organic C mg/l	Suspended Solids mg/l	Dissolved Metal $\mu\text{g/l}$			
				Zinc	Cadmium	Lead	Copper
11.07.84	127.5	35.0	7.1	787.0	3.07	90.0	347.6
01.08.84	1667.2	11.8	3.0	1110.8	3.1	162.0	327.8

The dissolved metal concentrations observed in the gullypot liquor will partly depend on the amount of metal which is contained in the interstitial sediment water before physical mobilisation (see Section 6.2.5) and partly on the extent of interstitial sediment water mobilisation. The dissolved and suspended solid metal species in the gullypot can then be released as a result of chemical and physical processes during a storm event.

#### 6.2.6.1 Controlling Parameters as Indicators of Metals Released from Interstitial Waters and Sediments.

Gullypot interstitial sediment water mobilisation is indicated by changes of controlling parameters such as conductivity, dissolved oxygen, redox potential, ATP and dissolved organic carbon. Only under very high flows is a significant amount of the gullypot sediment mobilised to such an extent that it is removed from the gullypot.

In large storm events the interstitial waters are disturbed at the beginning of the event. During this physical mobilisation process conductivity increases, due to the release of sediment associated salts, while dissolved oxygen decreases, due to oxygen utilisation by bacteria. Furthermore dissolved organic carbon increases, up to 41 mg/l in storm 6B and this is due to a great extent to the formation of sedimentary maturation products.

The increase of conductivity due to interstitial water mobilisation is rapid and the relative time of occurrence in the storm event can be related to the total storm road runoff volume (Table 6.13). Most of the storm events sampled had a high volume and therefore mobilisation primarily occurred at the beginning of the storm event. Notable exceptions occur where a high rainfall intensity is found for a very short period, such as in storm 6A, giving early interstitial water mobilisation for a relatively low total volume. However, changes in conductivity could provide a sensitive indicator of the time of mobilisation of dissolved metal enriched interstitial water during storm events.

Table 6.13 Occurrence of Conductivity Increase during Storm Events of Different Flow Volume.

Interstitial Water Mobilisation as Indicated by Conductivity, % Time of Storm Duration	Total Storm Flow Volume (litres)	Storm Events Sampled
<25%	>2000 *	6B, 6D, 6E, 6F
25-75%	1000-2000 †	6C
>75%	<1000 •	

\* 8 Events  
† 5 Events  
• 4 Events

For all the storms studied gullypot metal species in the Chelex Removeable fraction tend to follow conductivity, which is due to interstitial sediment water mobilisation. This is illustrated for Cu and Pb in storm 6C (Figure 6.13). In addition, at the beginning of the storm event there was an initial metal concentration peak which represents a rapid release of the most easily released sediment bound metal due to the initial low pH water contact.

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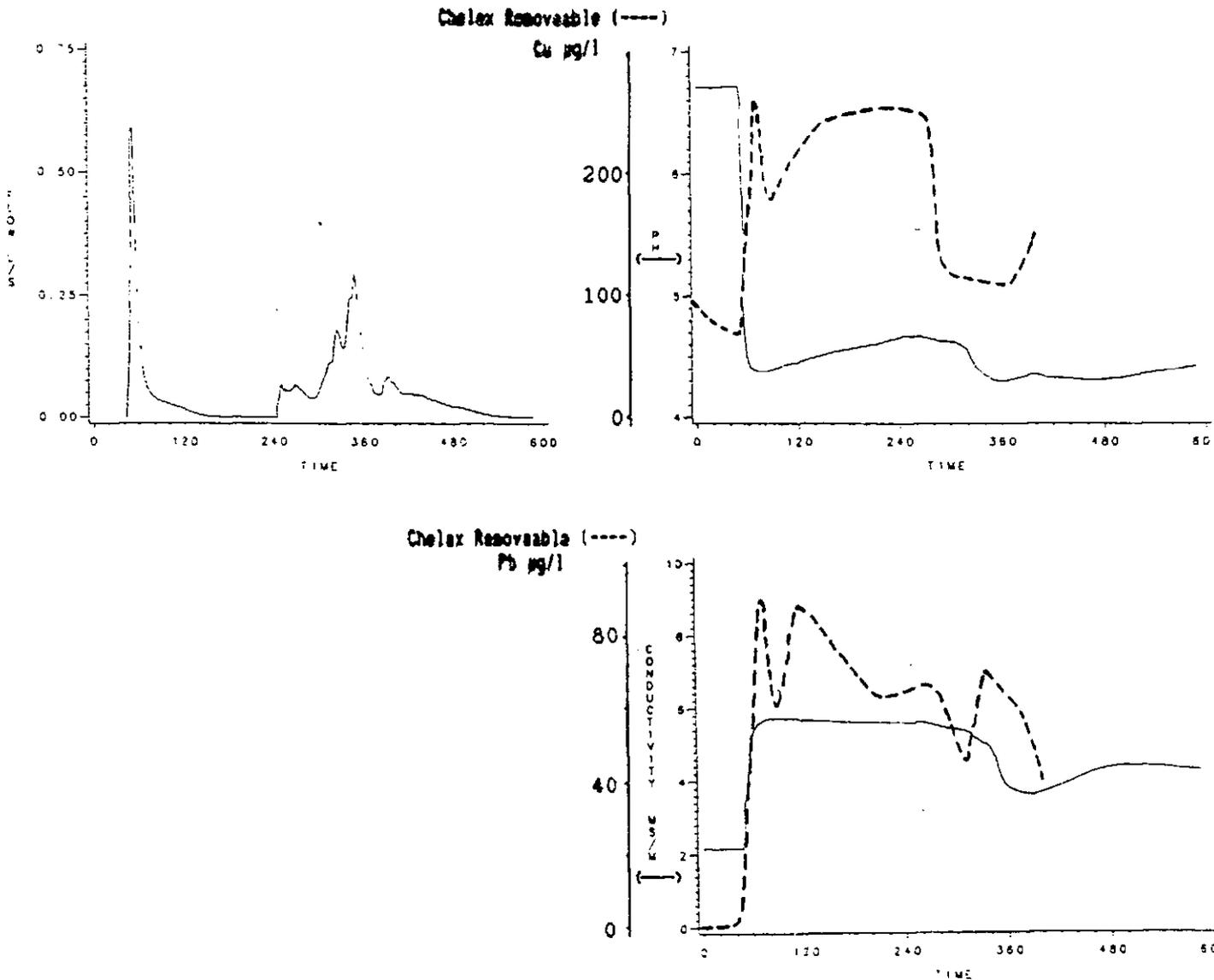


Figure 6.13 Gullypot Chelex Removeable Copper and Lead Concentrations  
 Compared to Controlling Parameters in Storm 6C.  
 Time in Minutes Commencing 08.00

Biological activity is also a significant feature of interstitial water mobilisation. The difference between the measured dissolved oxygen concentration and the expected saturation value is termed the Apparent Oxygen Utilisation (AOU). Incoming rainfall is expected to be

100% O<sub>2</sub> saturated and therefore the AOU (Figure 6.14) represents an instantaneous oxygen demand.

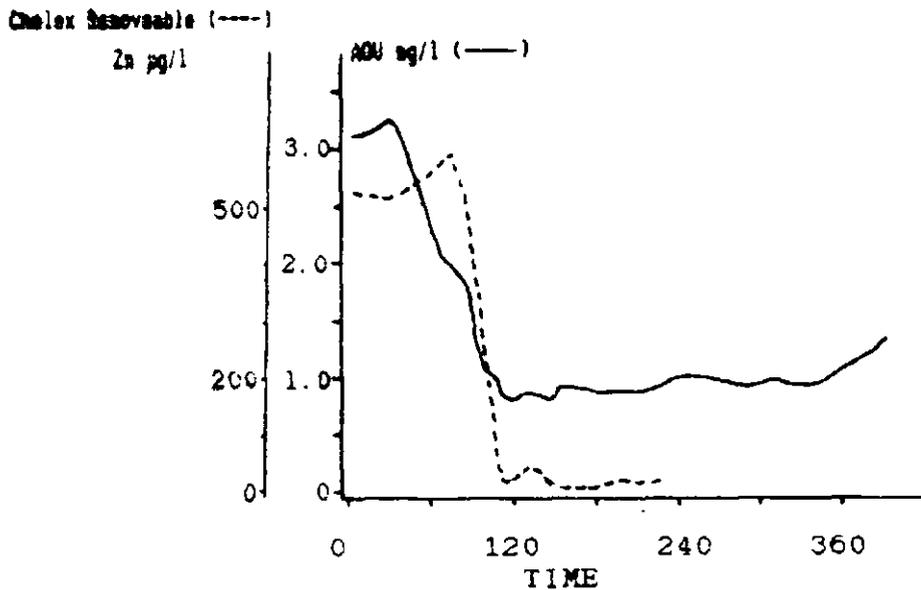


Figure 6.14 AOU and Chelex Removeable Zinc in the Gullypot, Storm 6B.  
Time in Minutes

The AOU therefore provides evidence of the gullypot interstitial water mobilisation. There may therefore exist some relationship between the AOU and dissolved metal species from the interstitial water. Chelex Removeable metals tend to follow the AOU profile, as seen for Zn in storm 6B, although a broader metal peak value is found and the gullypot sediment continues to exert an oxygen demand after the Chelex Removeable Zn is largely exhausted (for a comparison with conductivity and pH refer forward to Figure 6.18).

The gullypot liquor and interstitial water dissolved metal can be traced in the gullypot outflow when road runoff is also monitored, by superimposing the respective chemographs. Figure 6.15 shows the contribution of dissolved Pb and Cd to the gullypot outflow from the gullypot sediment and liquor. These profiles are typical for all four metals with a first important washout, due to gullypot liquor and

interstitial water, and further minor contributions later in the storm from interstitial water.

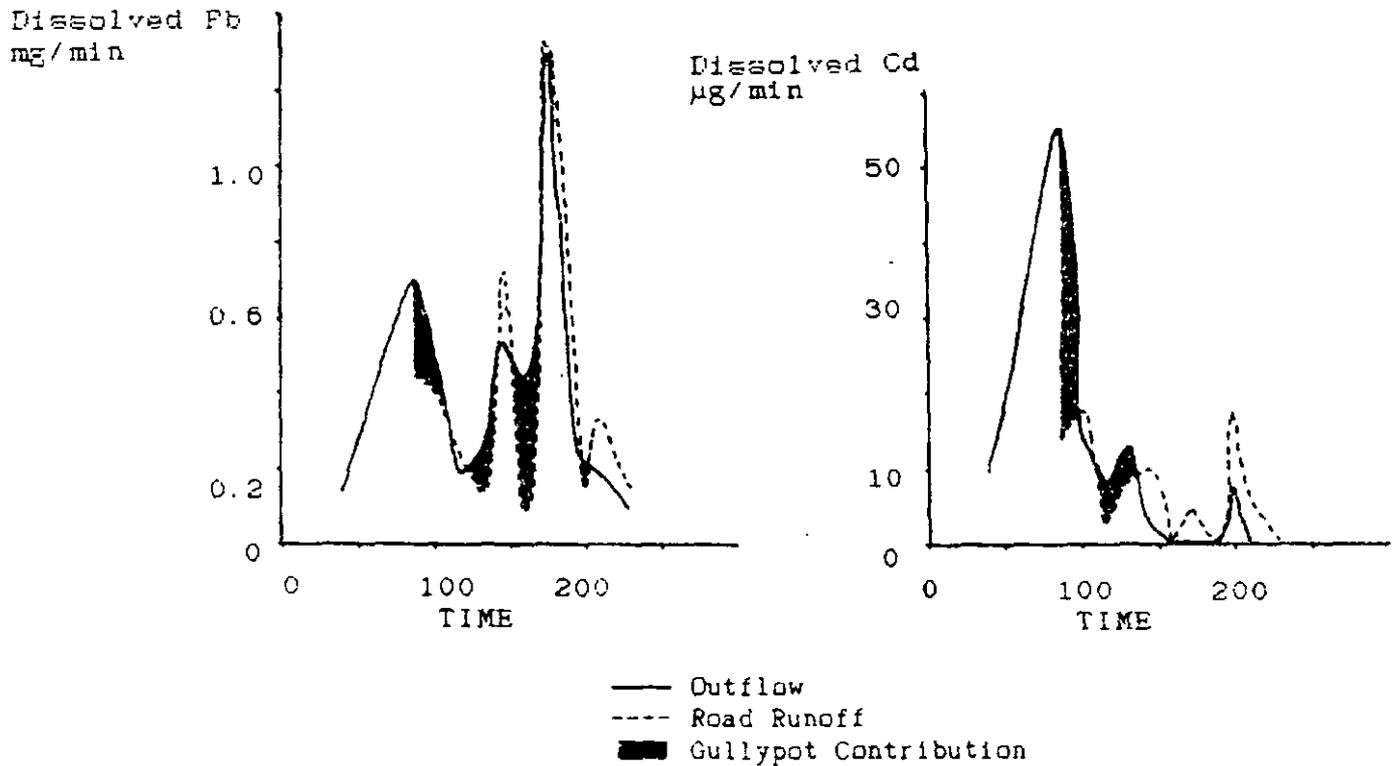


Figure 6.15 Superimposed Chemographs showing the Contribution of the Gullypot to Gullypot Outflow, Storm 6B.  
Time in Minutes

The release of metals into the gullypot outflow may also be traced using dissolved Ca loadings. Dissolved Ca can be acid washed from sediments in a similar way to metal ions. The cumulative chemographs are shown in Figure 6.16, comparing the Chelex Removeable metal fractions with Ca for storm 6B. Calcium shows a two-step profile which is followed by the metals, particularly Cu, indicating that probably the same mobilisation processes are in operation. The first step represents the influx of road runoff and washout of gullypot liquor, although in terms of mass balance road runoff accounts for 92.3% of the Ca and more than 72% of each metal. The second step represents the acid washing of gullypot sediments releasing a significant amount of inorganic Chelex Removeable metal species and salts.

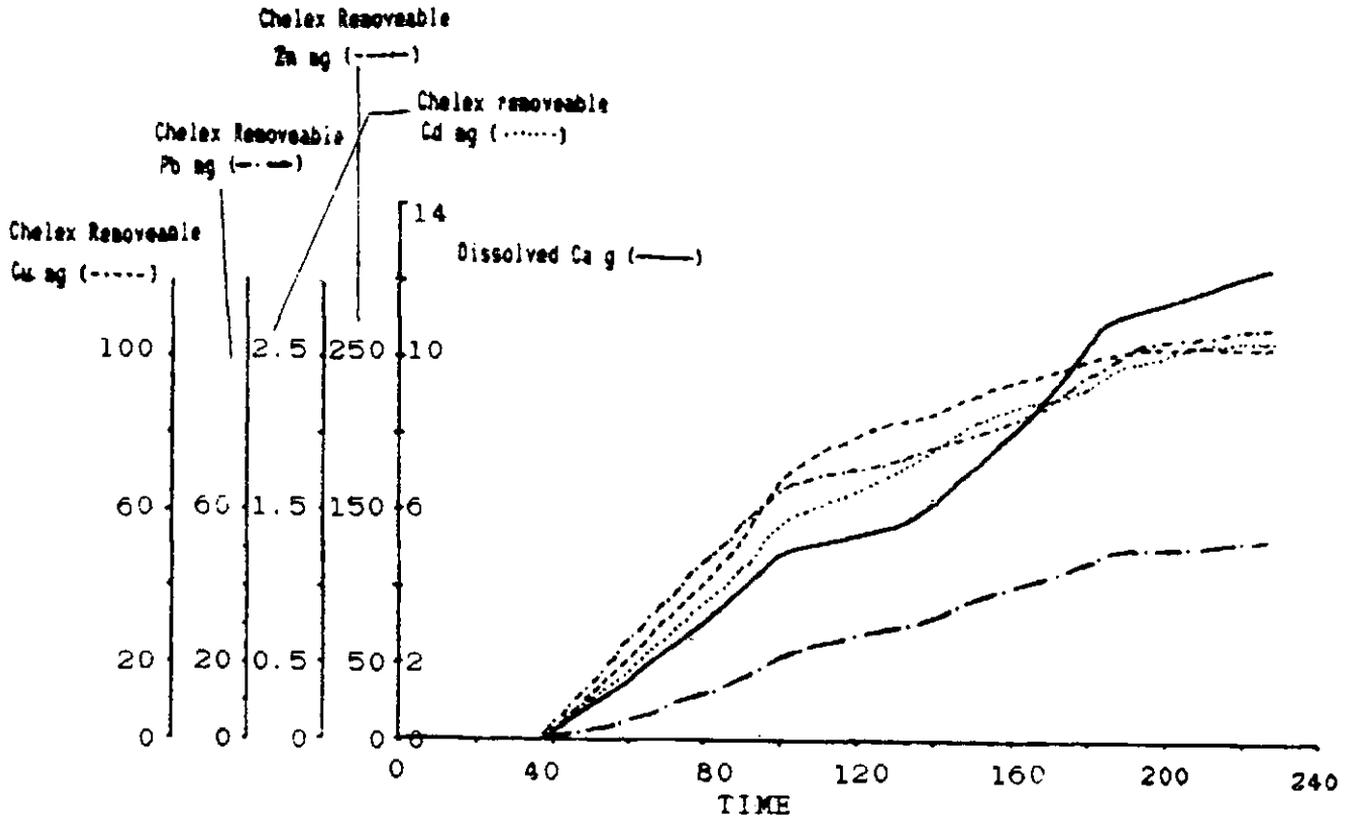


Figure 6.16 Cumulative Chemographs for Chelex Removeable Metals and Calcium, Storm 6B.  
Time in Minutes

#### 6.2.6.2 Gullypot Sediment Bound Metal Mobilisation.

A large storm with high volume and intensity is required to mobilise and wash out gullypot solids. Only in storms 6B and 6E was a significant removal of gullypot solids observed. During storm 6E the concentration of suspended solids in the gullypot reached 2145 mg/l and it is probable, with an incoming flow of 4.6 l/s (close to design capacity), that the gullypot contents were well mixed. Gullypot sediment mobilisation was not observed for storms 6C, 6D, and 6F. During these low flow events, with less than 50 mg/l of suspended solids leaving the gullypot, in terms of mass balance there is a net deposition of solids into the gullypot from road runoff. Therefore, during small storm events, the sediment metal outflow is largely the result of road runoff after certain heavy solids have settled in the gullypot sediment.

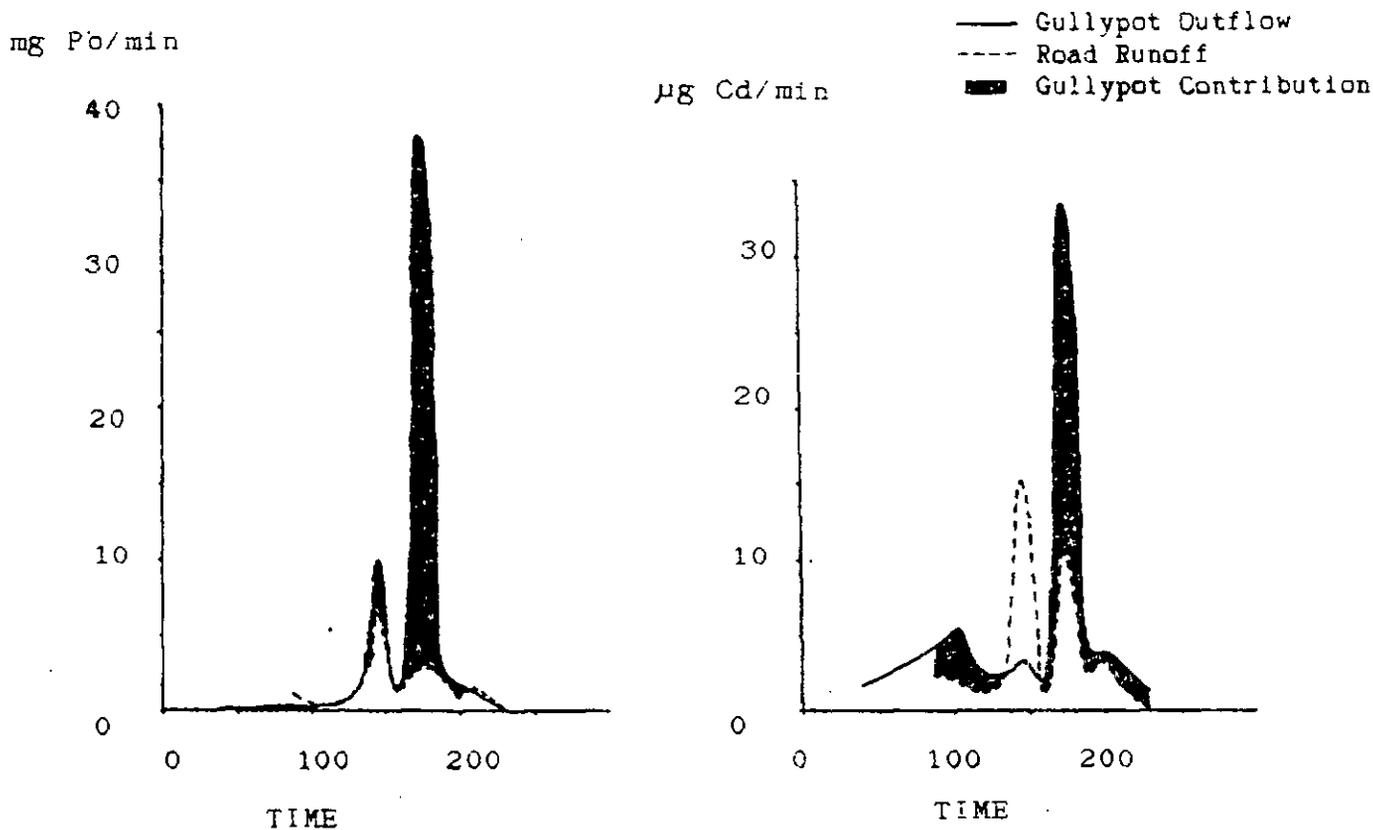


Figure 6.17 Superimposed Chemographs for Suspended Solid Lead and Cadmium, Storm 6B.  
Time in Minutes

Figure 6.17 shows the superimposed chemographs for suspended solid associated Pb and Cd during storm 6B which is a high flow storm event. These also reflect the chemographs for other monitored metals. In the case of Pb, during the first peak of Pb associated solids washoff, at 145 minutes, the gullypot only contributes a relatively small amount of Pb compared to road runoff. However, a secondary gullypot sediment mobilisation releases a much more significant amount of Pb to the storm sewer from the gullypot sediment. Most of this secondary loading peak contains Pb in the Exchangeable fraction.

Cadmium shows an early peak which may be related to highly enriched gullypot liquor suspended solids leaving the gullypot. Deposition of road solids in the gullypot sediment is occurring at 145 minutes, which are later remobilised and released at 173 minutes when a peak flow of 2 l/s enters the gullypot. Hence the gullypot contribution is increased by a short term storage of road solids. However, a mass balance for storm 6B shows that overall the gullypot contributes 0.45 mg of solid associated Cd to the total 1.0 mg leaving in the gullypot outflow.

### 6.3 Gullypot Outflow Pollutant Loadings.

Of the six storm events, whose general characteristics are outlined in Section 6.1, three storms provide enough data for an analysis of metal species leaving the gullypot outflow, i.e. 6B, 6D and 6E, with each storm event providing seven or more samples.

#### 6.3.1 Hydrographic and Controlling Parameter Variations.

The controlling parameter data collected for each storm can be analysed so that the character of each storm can be identified. Conductivity, pH, dissolved oxygen concentration and redox potential changes were continuously monitored in the gullypot, while dissolved organic carbon, dissolved Ca, suspended solids, particulate organic carbon and pH were also analysed for each sample in the gullypot outflow.

##### 6.3.1.1 Storm 6B.

This was a large volume (6932 litres) storm of 5.8 hours duration which was characterised by a long early flush of 1½ hours when the road runoff and initial gullypot liquor pollutants were to a great extent removed through the outflow. For dissolved pollutants this is indicated by continuous pH measurements (Figure 6.18) which have fallen to close to typical rainfall levels after 1½ hours (rainfall pH of this event = 4.1). This shows that dissolved buffering agents have

become depleted after 1½ hours. Redox potential decrease, dissolved oxygen depression and an increase of conductivity suggest that during the first two hours the interstitial sediment waters are mobilised and mixed with outflowing gullypot water.

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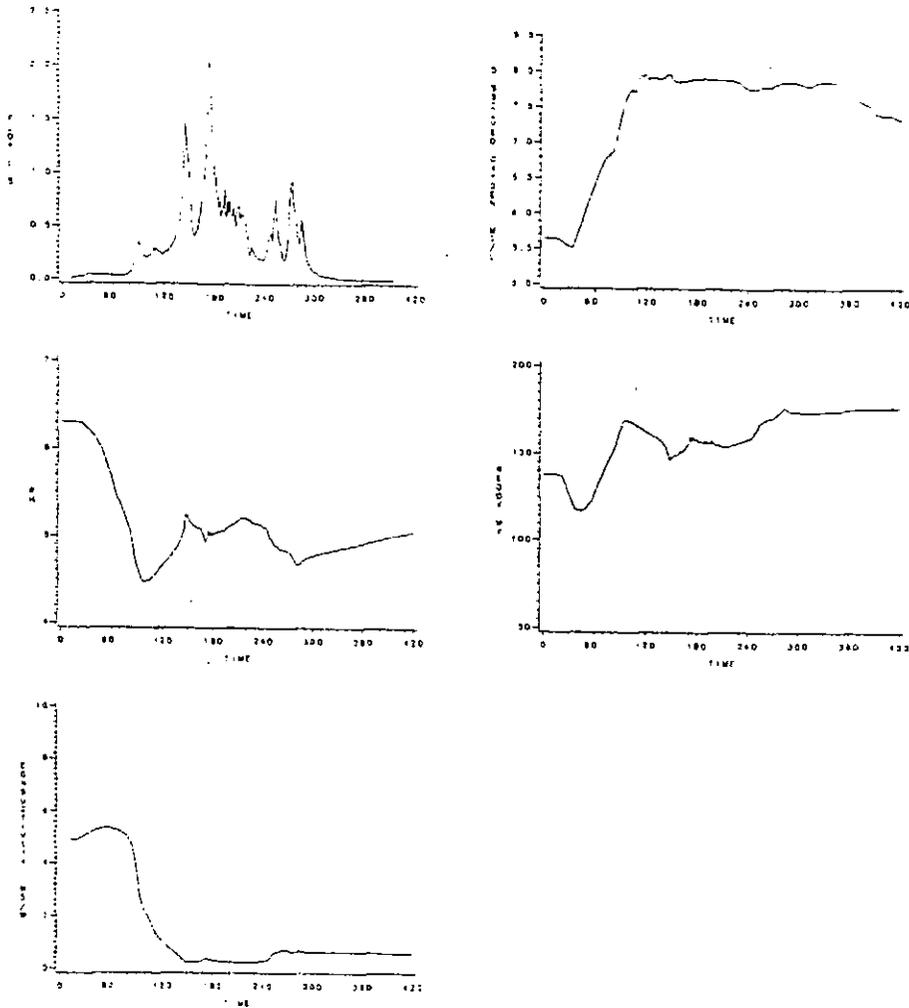


Figure 6.18 Variations of Controlling Parameters, Storm 6B. Time in Minutes Commencing 09.00.

After two hours the rainfall intensity increased and during the resulting high flow, which reached 2 l/s, the gullypot solids were mobilised (Figure 6.19) resulting in a large discharge of solids. The

associated drop in redox potential suggests that further interstitial water was mobilised as well (Figure 6.18). The loading pattern for particulate organic carbon follows the same trend as suspended solids (Figure 6.19). However, in the early and later stages of the storm, incoming road runoff solids (14-27% particulate organic carbon composition) and gullypot liquor solids (21% particulate organic carbon composition) enrich the chemograph for particulate organic carbon. During the mobilisation of the organic deficient basal sediments (7% particulate organic carbon composition) between 130 and 190 minutes, the particulate organic carbon storm profile is lowered compared to suspended solids (Figure 6.19).

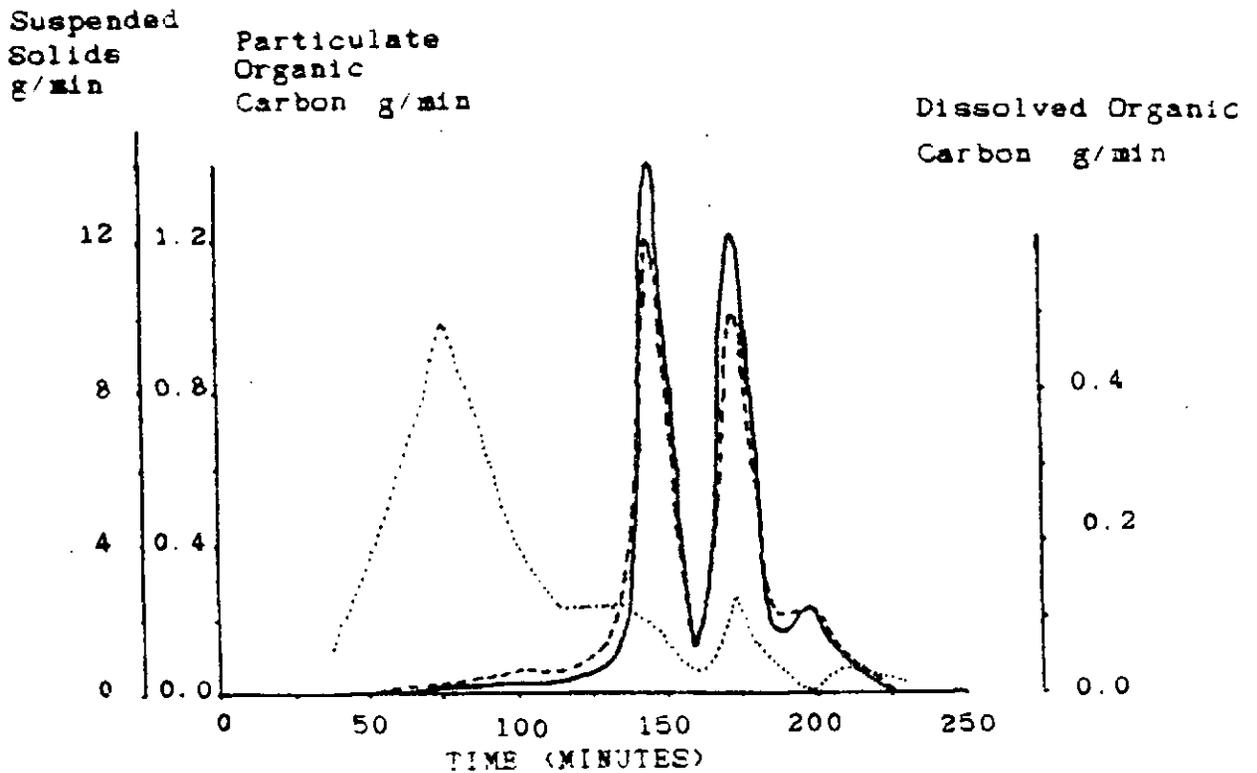


Figure 6.19 Parameter Loadings, Storm 6B.

Dissolved organic carbon is predominantly washed out in the first low flow stage of the storm (Figures 6.18 and 6.19), with a similar profile for dissolved Ca (not shown). The first dissolved organic carbon peak is a combination of the washout of dissolved organic

carbon in road runoff, gullypot liquor and sediment interstitial water. The further washout at 173 minutes is solely derived from a road runoff contribution.

6.3.1.2 Storm 6D.

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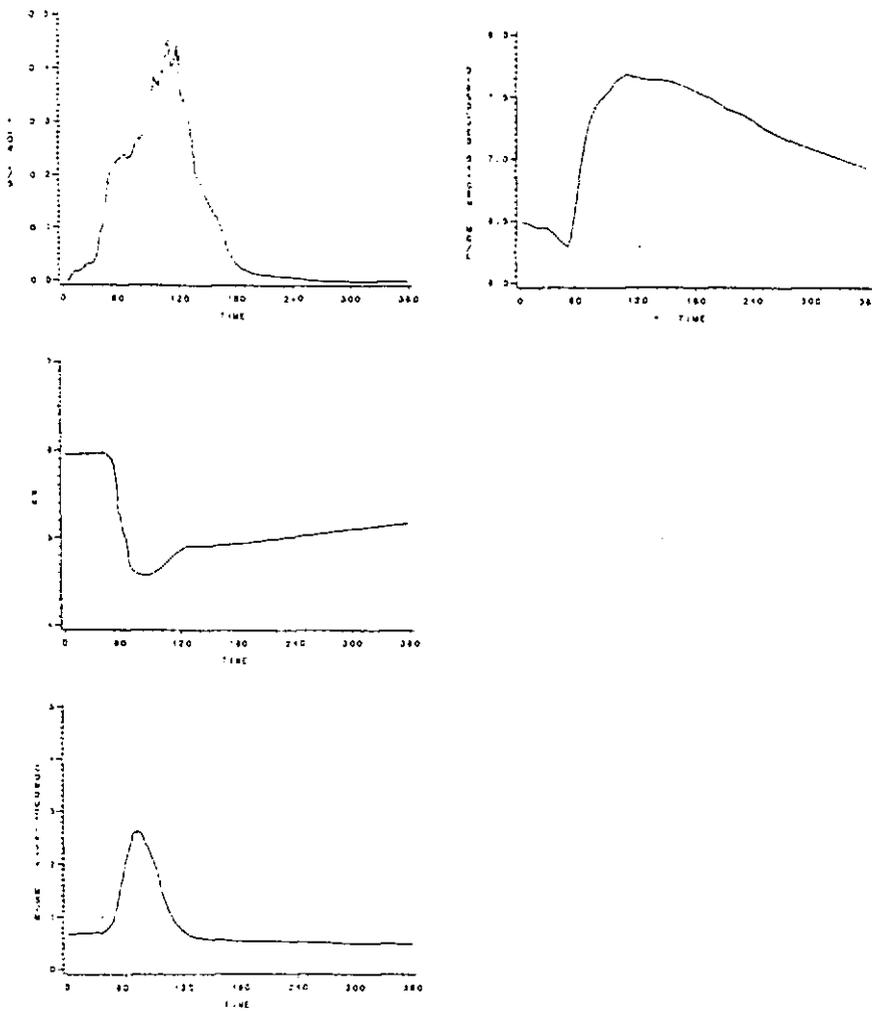


Figure 6.10 Variations of Controlling Parameters, Storm 6D. Time in Minutes Commencing 07.00.

This was a low intensity storm of just over three hours duration and a road washoff volume of 2155 litres. The road runoff flow increases slowly over the first two hours and then decreases rapidly after the peak of 0.45 l/s (Figure 6.20). The gullypot sediment was not significantly mobilised by this storm event and therefore suspended solid loadings were dominated by road runoff. However, the sediment interstitial water is released into the gullypot as indicated by the dissolved oxygen depression and increase in conductivity (Figure 6.20).

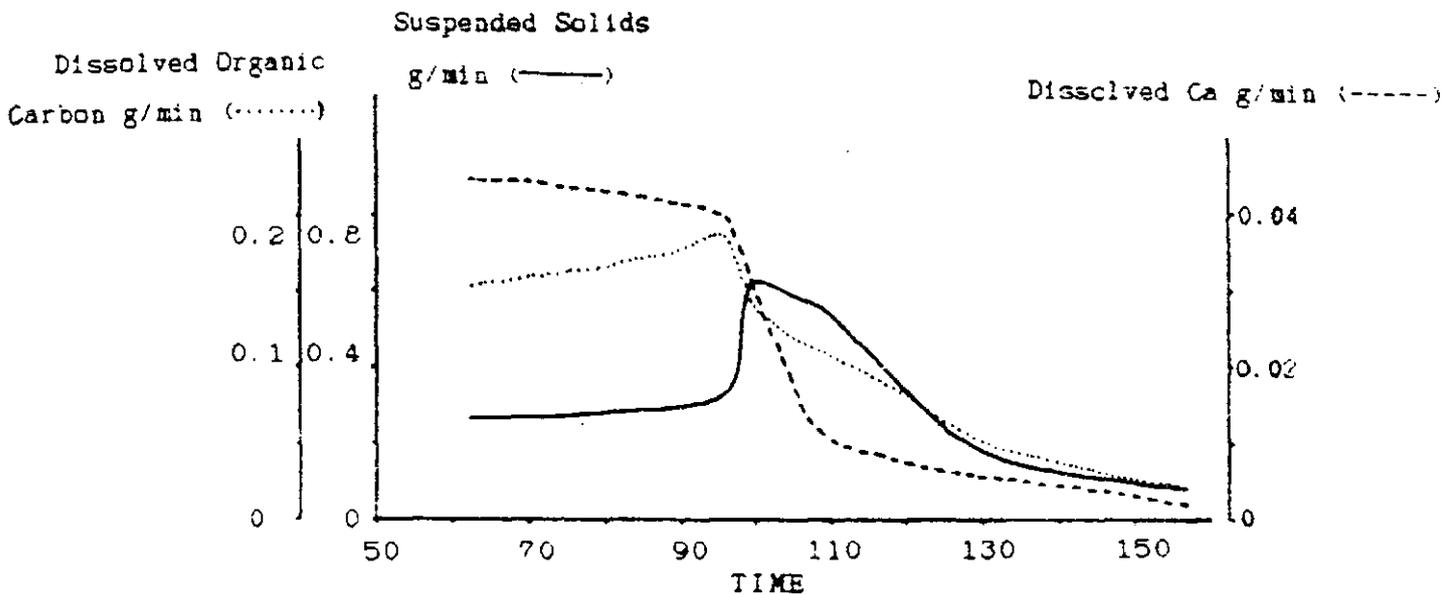


Figure 6.21 Parameter Loadings, Storm 6D.  
Time in Minutes

The suspended solids peak loading in the outflow precedes peak flow (Figure 6.21) although the road runoff is characterised by a distinct solids "first flush". It may be that the gullypot is acting as a temporary detention basin for these road solids before releasing them immediately, under slightly higher flow conditions, on the rising limb of the hydrograph.

Dissolved organic carbon is released from the gullypot as a prolonged "first flush", representing a release of dissolved organic carbon from road runoff, gullypot liquor and sediment interstitial waters. Dissolved Ca shows a more defined "first flush", although originating from the same sources, than dissolved organic carbon. This was consistently observed in all the storms studied and suggests that Ca is readily dissolved and inert to chemical changes through the gullypot system. However, dissolved organic carbon may undergo continued sediment/water interactions, such as a slow release of organics from gullypot sediment.

6.3.1.3 Storm 6E.

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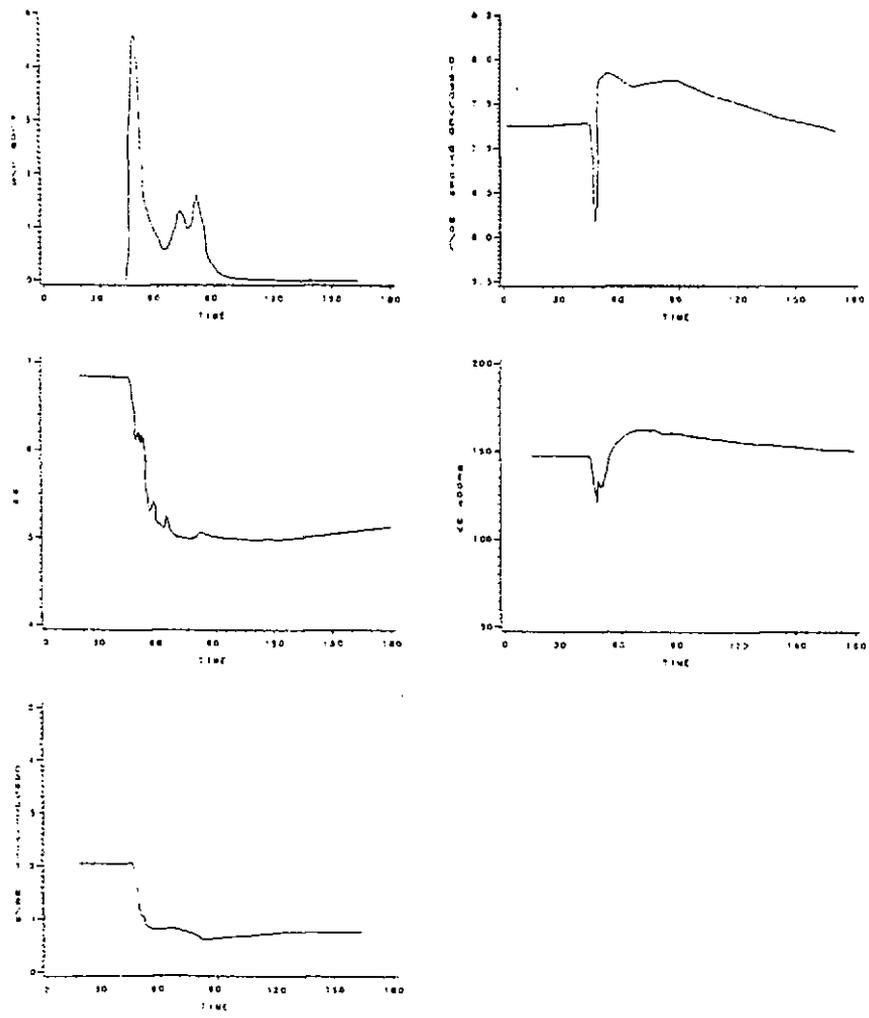


Figure 6.22 Variations of Controlling Parameters, Storm 6E. Time in Minutes Commencing 10.00.

Storm 6E was a heavy thunderstorm of 1½ hours duration. The incoming flow to the gullypot reached a value of 4.6 l/s which is close to the design capacity (Figure 6.22). The controlling parameters in the gullypot; conductivity, pH, dissolved oxygen and redox potential, suggest that the gullypot liquor and interstitial water are washed out after 5-10 minutes. This is characterised by a sharp inverse deficit peak for dissolved oxygen.

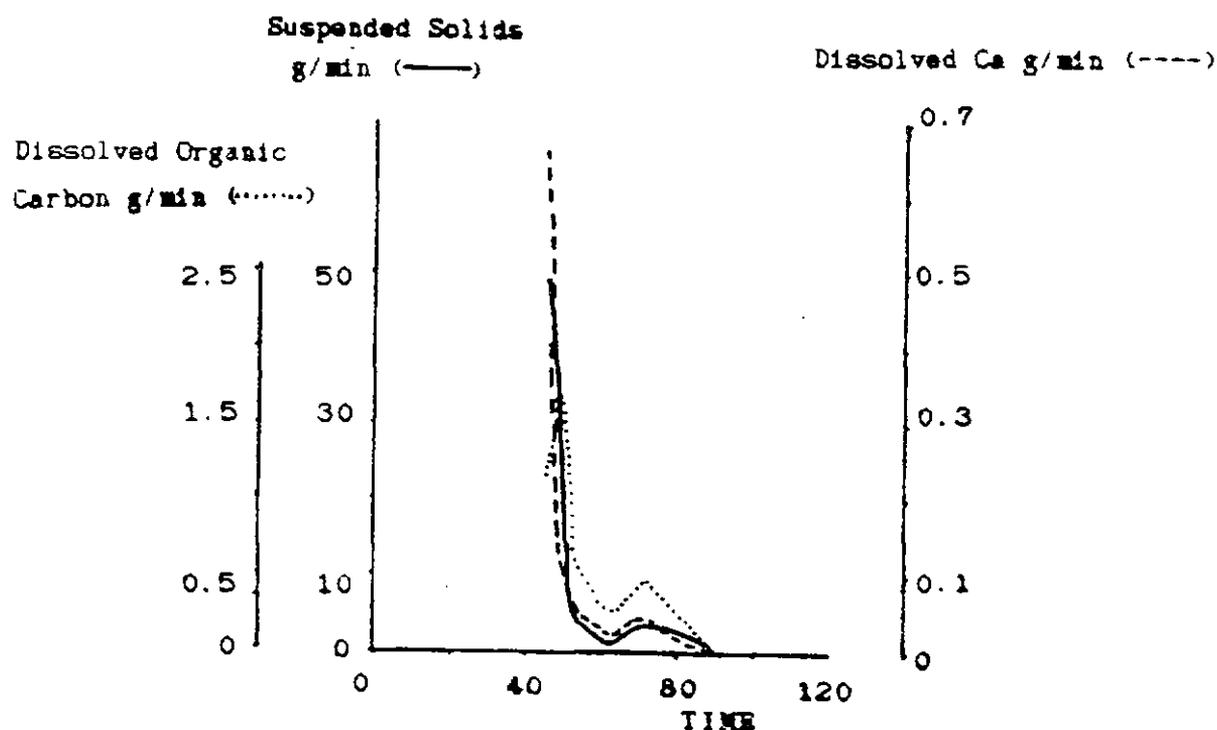


Figure 6.23 Parameter Loadings, Storm 6E.  
Time in Minutes

Figure 6.23 shows that both dissolved and suspended solid components are rapidly washed out of the gullypot with "first flushes" for suspended solids, as well as dissolved Ca, on the rising limb of the hydrograph. Particulate organic carbon (not shown) has a similar profile to suspended solids, but the percentage of solids as organic carbon in the gullypot (1.1-8.2%) is lower than in the gullypot outflow (5.4-11.8%). This suggests that either highly organic road runoff solids overtop the gullypot during such a high intensity storm, or more probably that the dynamic mixing of the gullypot by the high

energy incoming water stirs up the basal sediments, of which only the lighter more organic particles are discharged through the outflow.

Dissolved organic carbon again shows a different profile with a peak following maximum flow (Figure 6.23). At this point the gullypot basal sediment seems to have been completely mixed (to give 2145 mg/l suspended solids) and the dissolved organic carbon peak may be due to the mechanical washing of organic compounds from the suspended basal sediment.

A second peak for all constituents is found on the rising limb of a second intense shower of up to 1.6 l/s (Figure 6.22). However, there is obviously a dilution-exhaustion of controlling parameters after the first event.

### 6.3.2 Loading Variations for Metals and Metal Species.

Not only will gullypot outflow metal species loading variations be considered in this section, but wherever possible the origin of important metal species peaks will be determined by comparing road runoff and outflow hydrographs. In some cases metal species follow the hydrographs and controlling parameters discussed in Section 6.3.1, but deviations can often be explained in terms of the physical and chemical processes discussed in 6.2. A notable example is that of dissolved metals which usually follow the "first flush" pattern observed for dissolved organic carbon. However, dissolved metals also frequently show further and sometimes even greater, secondary loading peaks which are not observed for dissolved organic carbon. This can be attributed to the acid rain washing of road surface, as well as gullypot, sediments which releases dissolved metals, but not dissolved organic carbon. It should be noted in subsequent sections that the Electrochemically Available and Chelex Removeable fractions usually peak together and cannot be separated in terms of different origins and processes.

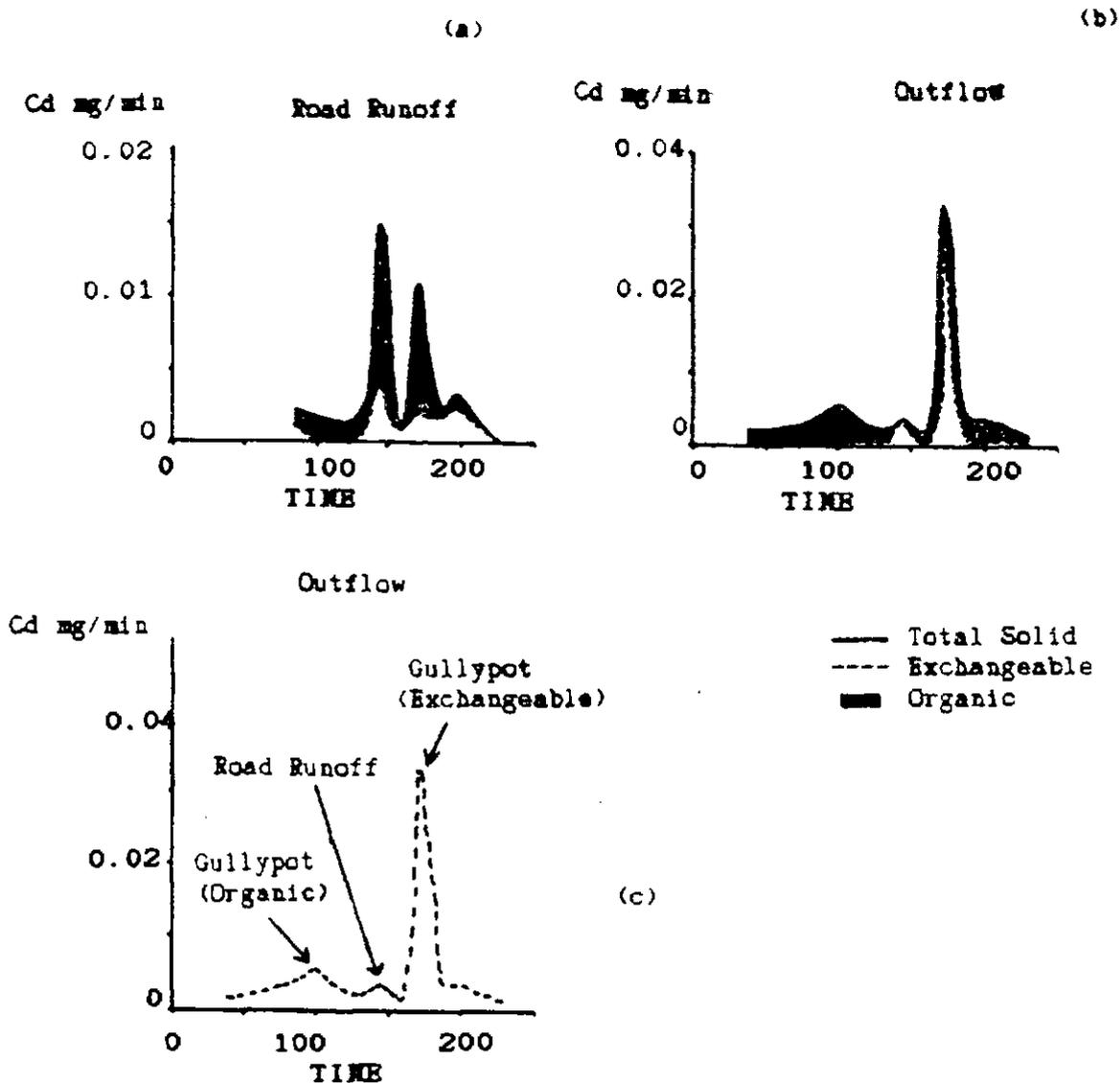


Figure 6.24 Loading Variations of Suspended Solid Cadmium Species in Road Runoff and Gullypot Outflow.  
Time in Minutes

To illustrate the approach used to determine the origin of dominant metal species the loading variations of suspended solid Cd species in storm 6B are considered (Figure 6.24). The road runoff entering the gullypot mostly contains the Organic fraction during the early and middle stages of the storm event. The Cd peak in gullypot outflow at 145 minutes can be attributed to road runoff (Figure 6.24(a) and (c)). The gullypot contributes significant loadings of suspended solid Cd

throughout storm 6B. In the early stages of the storm the gullypot liquor dominates the gullypot outflow which mostly contains Organic Cd (Figure 6.24(a) and (c)). The peak at 173 minutes is due to the mobilisation of gullypot sediments and is largely Exchangeable in character.

#### 6.3.2.1 Dissolved Zinc Fractions.

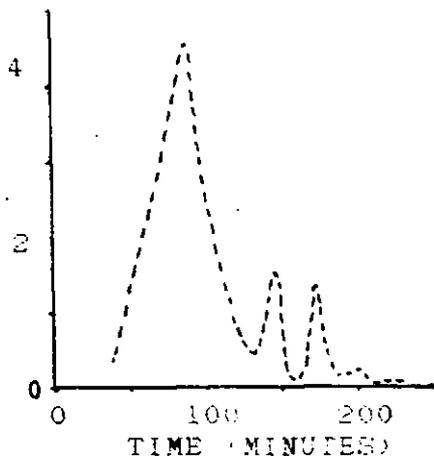
Dissolved Zn profiles for the gullypot outflow are dominated by Chelex Removeable metal.

For storm 6B (Figure 6.19 and Figure 6.25(a)), the Chelex Removeable profile follows dissolved organic carbon, with the same "first flush" peak representing the early washing of road surface sediments, gullypot liquor and interstitial sediment water. Two late peaks are found which correspond to flow peaks and can be related to the acid washing of road and gullypot sediment resulting in the release of dissolved Zn.

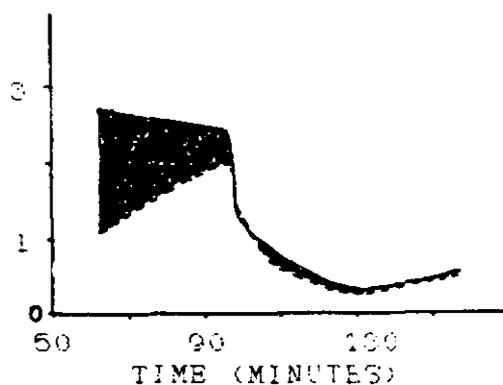
In storm 6D (Figure 6.20 and Figure 6.25(b)), Strongly Bound Zn makes a significant addition to the early part of the chemograph; the rest of the profile being dominated by Chelex Removeable Zn. The early Strongly Bound Zn loading is from the gullypot liquor which often contains a significant amount of Strongly Bound Zn.

During storm 6E (Figure 6.22 and Figure 6.25(c)), the Chelex Removeable Zn is discharged as a broad "first flush" in a similar way to dissolved organic carbon. The significant secondary Chelex Removeable Zn peaks lag behind the other controlling parameters and may be due to the further acid rain washing of road and gullypot sediments.

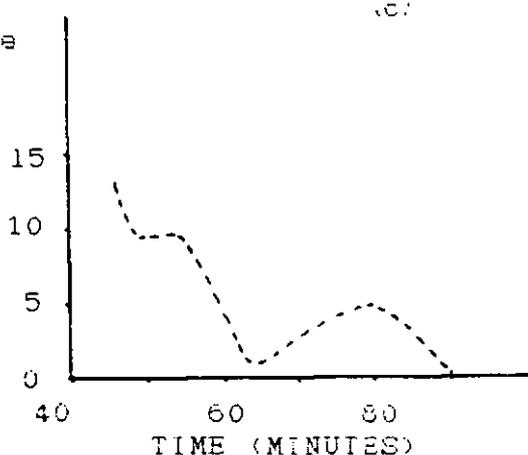
Chelex  
Removeable  
Zinc  
mg/min



Total  
Dissolved  
Zinc  
mg/min



Chelex  
Removeable  
Zinc  
mg/min



— Total Dissolved  
- - - Chelex Removeable  
■ Strongly Bound

Figure 6.25 Dissolved Zinc Loading Variations for Gullypot Outflow.

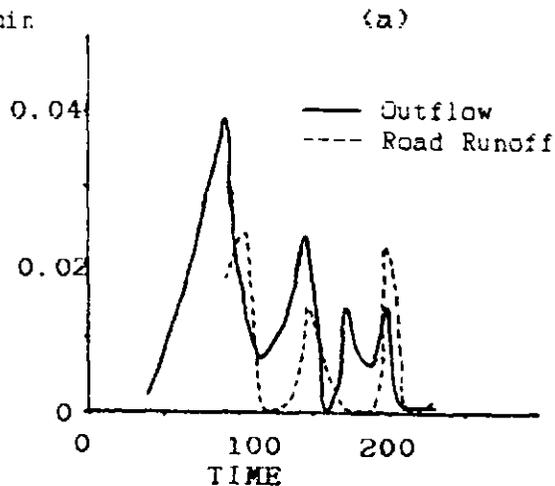
### 6.3.2.2 Dissolved Cadmium Fractions.

The dissolved Cd profiles are dominated by Chelex Removeable species, but inputs of the Strongly Bound fraction are a useful indicator of gullypot liquor and interstitial sediment water leaving the gullypot. In addition there is evidence of acid rain mobilisation (see Section

6.2.2.1) increasing dissolved, and in particular Chelex Removeable, Cd levels.

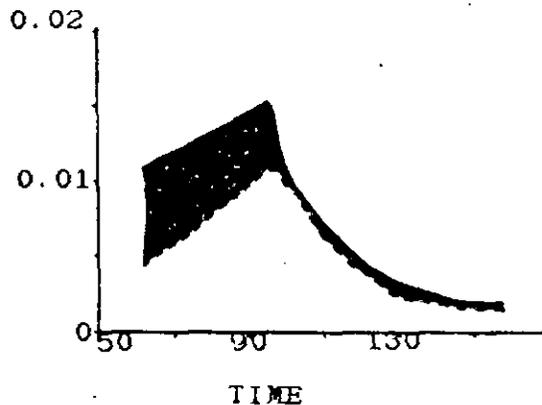
Chelex Removeable

Cd mg/min



Total Dissolved

Cd mg/min



Total Dissolved

Cd mg/min

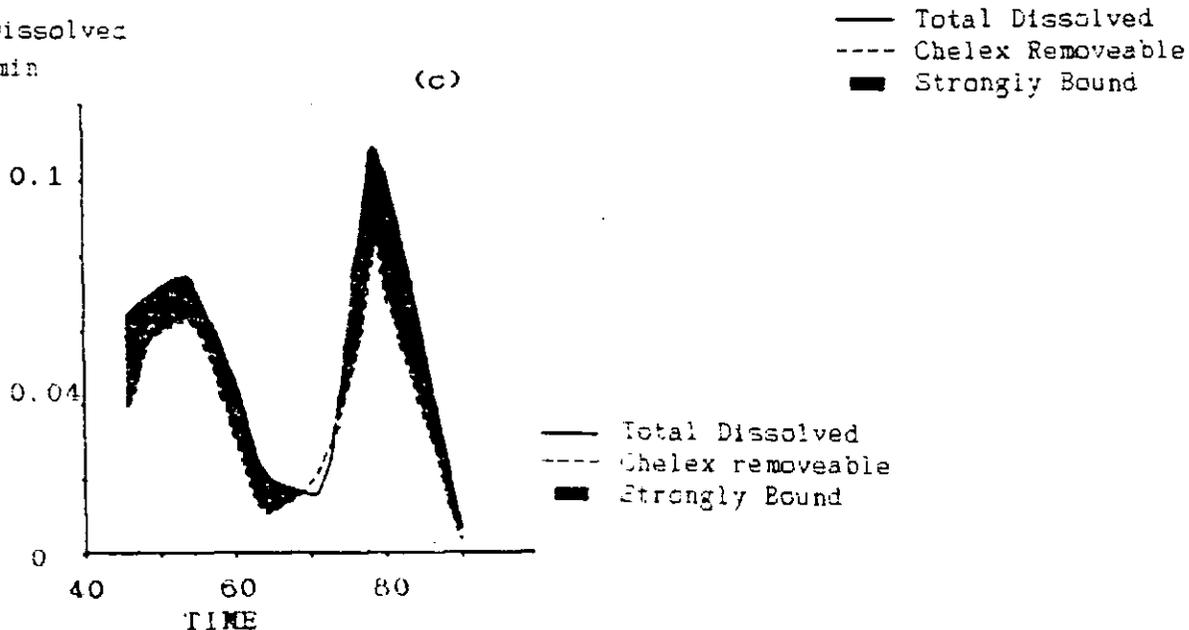


Figure 6.26 Dissolved Cadmium Loading Variations for Gullypot  
Outflow.  
Time in Minutes

For storm 6B (Figure 6.19 and Figure 6.26(a)) Chelex Removeable Cd dominates the storm chemograph, except at the very beginning of the storm (10-60 minutes) where the Strongly Bound fraction contributes up

to 70% of the gullypot outflowing dissolved Cd. This is due to Cd complexation by organic compounds originating from the gullypot liquor and gullypot interstitial sediment water, as well as the road surface. The first Chelex Removeable gullypot outflow Cd peak (Figure 6.26(a)) follows dissolved organic carbon washout (Figure 6.19). The superimposed road runoff Chelex Removeable Cd shows that road runoff is an important source of Chelex Removeable Cd, probably due to acid rain mobilisation. However, gullypot liquor and interstitial sediment water contributes the excess Chelex Removeable Cd. Acid rain mobilisation (see Section 6.2.2.1) of sedimentary bound Cd and transportation as Chelex Removeable Cd produces the late peaks found in storm 6B, which are not found for dissolved organic carbon. The gullypot outflow peak at 173 minutes can be attributed to the acid washing of suspended and basal gullypot sediments; the gullypot basal sediments are being mobilised at this point (Figure 6.19) and therefore can readily contribute acid rain solubilised Cd. The peaks at 145 and 197 minutes, as seen by the road runoff peak, are mainly due to the acid washing of road sediments.

In storm 6D (Figure 6.20 and Figure 6.26(b)) Chelex Removeable Cd again tends to dominate the dissolved metal profile. The low profile of this storm (Figure 6.19) contributes to a prolonged "first flush" of dissolved constituents. Correspondingly the same prolonged "first flush" is also seen for dissolved Cd. The significant contribution of Strongly Bound Cd to this early part of the storm shows that the gullypot liquor and interstitial sediment water are important contributors of dissolved Cd. During the rest of the storm the profile is dominated by Chelex Removeable Cd, suggesting that acid rain mobilisation by dissolution of Cd from road and gullypot sediments is most important.

The importance of the Strongly Bound fraction during early discharge was also seen in storm 6E (Figure 6.26(c)). Therefore, even in intense events metal species arising from the gullypot liquor and interstitial sediment water are observable in the outflow chemographs. Despite the obvious dilution-exhaustion of controlling parameters for the second

thunderstorm flow peak (Figure 6.23) a larger Chelex Removeable Cd peak is observed at this stage. During the first part of the storm the pH fell from 6.9 to 5.5, however during the second stage of the storm the pH fell to around pH 5.0. Therefore the acid washing of sediments to remove Chelex Removeable Cd increased in the second part of the storm and there is clearly more Cd available for acid mobilisation than for early storm solubilisation at near neutral pH values.

6.3.2.3 Dissolved Lead Fractions.

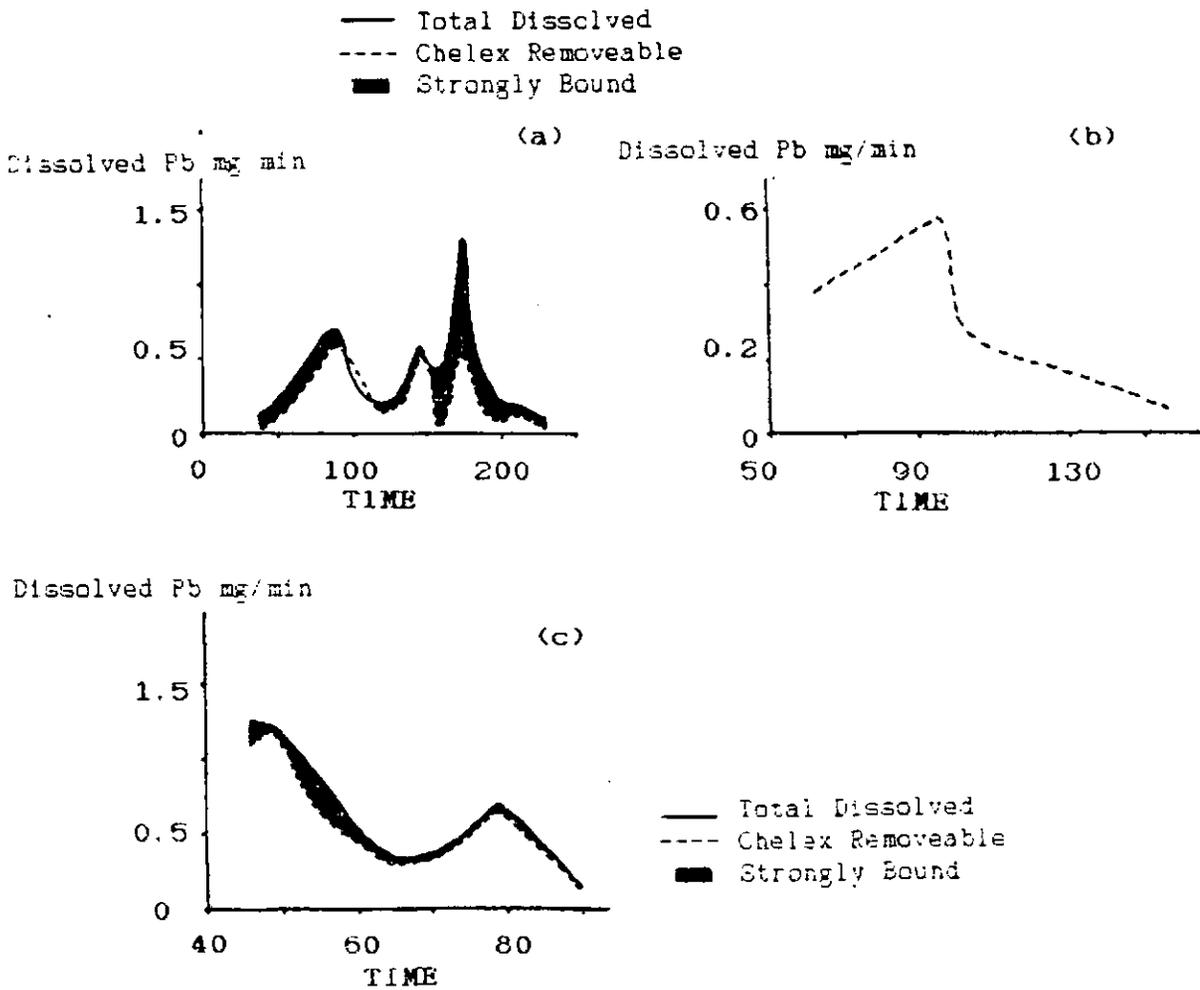


Figure 6.27 Dissolved Lead Loading Variations for Gullypot Outflow.  
Time in Minutes

Dissolved Pb profiles are similar to dissolved Cd in being dominated by Chelex Removeable species. Acid rain mobilisation is also an important process throughout storm events for the dissolved form of this metal.

Storm 6B (Figure 6.19 and Figure 6.27(a)) shows a first dissolved Pb peak due to the solubilisation of Pb from road surface sediments, as well as from gullypot liquor and interstitial sediment water. Only a small proportion of the Pb is in the Strongly Bound form at the beginning of the storm. Secondary peaks can be attributed to the acid washing of sediments, particularly those on the road surface, yielding significant loadings of Chelex Removeable Pb. Most of the Strongly Bound metal is released late in the storm event. A late peak is also seen for dissolved organic carbon (Figure 6.19) which originates in the road runoff. It may therefore be that the acid washing of road solids releases Chelex Removeable Pb, a significant proportion of which is complexed by specific organic compounds also transported in the road runoff.

Most of the dissolved Pb in storm 6D (Figure 6.20 and Figure 6.27(b)) is derived from road runoff and is in the Chelex Removeable fraction. The loading profile for total dissolved Pb follows dissolved controlling parameters such as dissolved organic carbon and dissolved Ca with a long "first flush" washout.

A similar trend of dissolved Pb washout is seen in storm 6E, Figure 6.23 and Figure 6.27(c), with most of the metal in the Chelex Removeable fraction, although the Strongly Bound fraction is observable at the beginning of the storm. The second significant peak which is found, despite a noticeable dilution-exhaustion of dissolved organic carbon, can be related to the further acid washing of road and gullypot sediments at pH 5.0 (as was discussed for dissolved Cd).

#### 6.3.2.4 Dissolved Copper Fractions.

Dissolved Cu is mostly present in the Chelex Removeable fraction, but the Strongly Bound fraction is significant when the gullypot contents are mobilised.

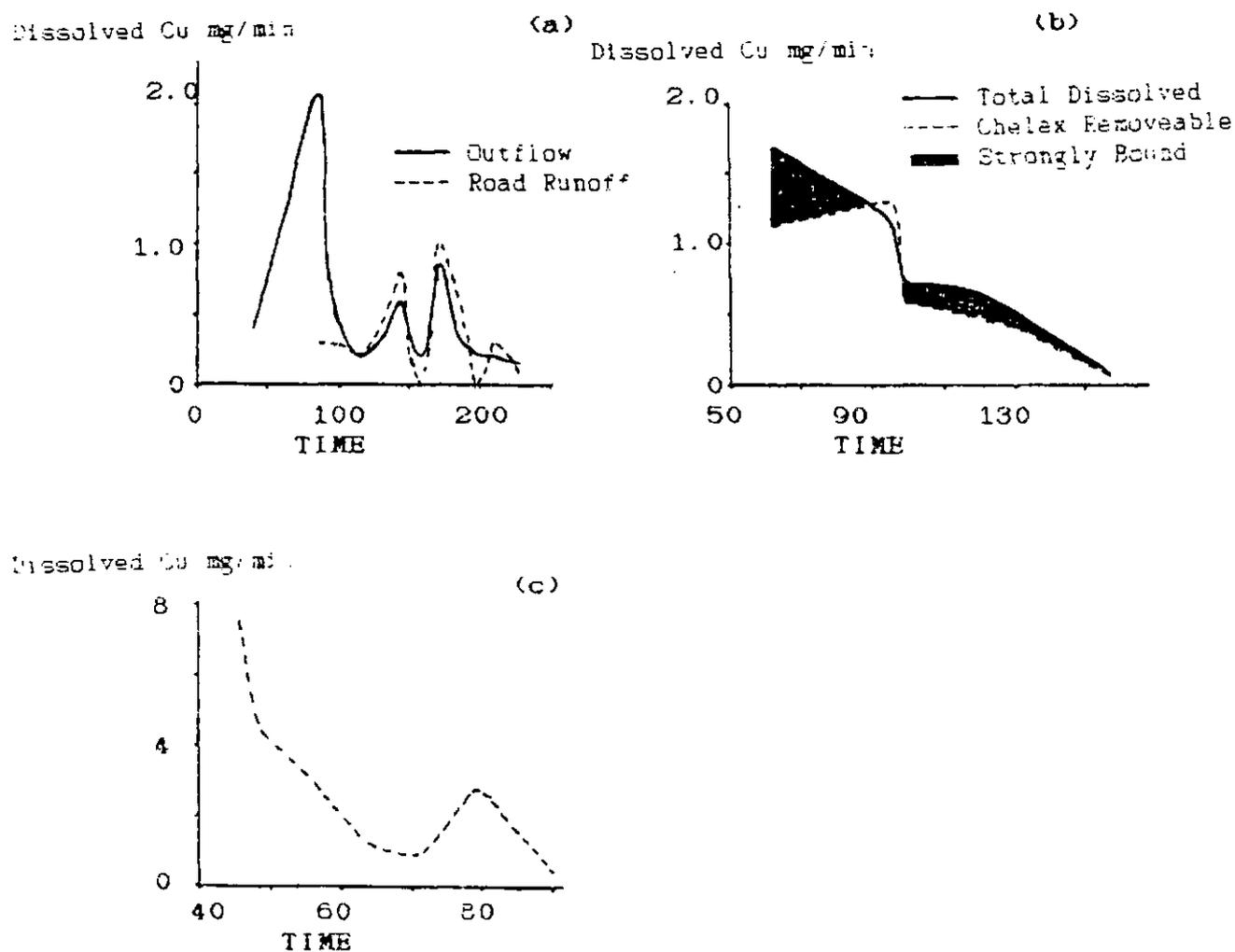


Figure 6.28 Dissolved Copper Loading Variations for Gullypot Outflow.  
Time in Minutes

For storm 6B (Figure 6.19 and Figure 6.28(a)) Chelex Removeable Cu dominates the profile, with the Strongly Bound fraction (not shown) only significant at the very beginning of the outflow. The gullypot liquor and interstitial sediment water are more important than road runoff, for dissolved Cu, at the commencement of storm 6B. At the onset of runoff the increase in dissolved Cu due to sediment maturation, by the process described in 6.2.5, had reached 347.6 µg/l (100% as Chelex Removeable Cu). This meant that at least 14.4 mg of dissolved Cu was available in the gullypot liquor, which corresponds to much of the difference between the road runoff and gullypot outflow loadings in Figure 6.28(a). The remaining Cu is due to interstitial sediment water mobilisation. The final two dissolved Cu peaks, corresponding to peak flow, are totally due to road runoff. Therefore the acid rain washing of sediment to dissolve Cu late in this storm event is important for the road sediments, but not for the gullypot sediments.

During storm 6D (Figure 6.20 and Figure 6.28(b)) the gullypot contributes most of the dissolved Cu to the outflow. Consequently during this low flow storm the Strongly Bound Cu, probably derived from interstitial water mobilisation, is important until 100 minutes when both dissolved organic carbon and dissolved Cu decrease.

Total dissolved Cu in storm 6E (Figure 6.23 and Figure 6.28(c)) has a similar profile to the other dissolved metals for this storm, with a significant "first flush" related to readily solubilised Cu from road sediments and dissolved Cu from the gullypot liquor and interstitial sediment water. The second peak is due to the acid rain washing of road and gullypot sediments.

#### 6.3.2.5 Suspended Solid Zinc Fractions.

In road runoff the Exchangeable Zn fraction is most important for suspended solids. However, in the gullypot outflow the Carbonate and Hydrrous Metal Oxide fraction dominates, probably due to redox/surface area dependent Zn uptake onto solids in the gullypot. The Organic

fraction may provide a useful indication of fine sediment mobilisation in the gullypot.

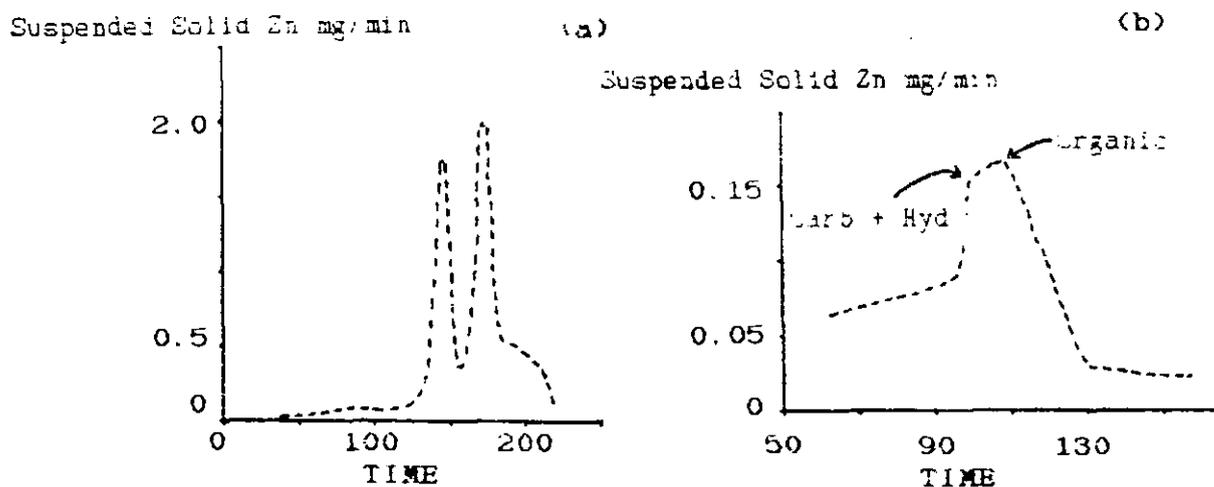


Figure 6.29 Suspended Solid Zinc Loading Variations for Gullypot Outflow.  
Time in minutes

Particulate associated Zn fractions tend to follow suspended solid loadings as in storm 6B (Figure 6.19 and Figure 6.29(a)). Therefore the two significant peaks are related to the mobilisation of gullypot solids giving a large discharge of the Carbonate and Hydrous Metal Oxide Zn fraction. This metal fraction may be formed during the contact of disturbed reduced bottom sediments with incoming oxygenated road runoff. Under such conditions Fe(III) and Mn(IV) may precipitate as the respective hydroxides, co-precipitating and adsorbing dissolved Zn species at the same time. This suggests the action of a redox/surface area dependent metal uptake mechanism (see 6.2.4).

In storm 6D (Figure 6.20 and Figure 6.29(b)) the Carbonate and Hydrous Metal Oxide Zn fraction again follows suspended solid loadings. However, the Organic Zn fraction gives rise to a late peak for total solid Zn. As this fraction was not found to be significant in road runoff solids, it can be attributed to the mobilisation of fine

organic solids at the gullypot sediment/liquor interface. This is supported by the increase of particulate organic carbon from 1.4%, at the beginning of the storm event, up to the 10.7% found at the Organic Zn fraction peak.

#### 6.3.2.6 Suspended Solid Cadmium Fractions.

Suspended solid Cd shows a complex relationship between the Exchangeable and Organic fractions, depending on flow and controlling parameter conditions. The Carbonate and Hydrous Metal Oxide Cd fraction was never in detectable concentrations during the gullypot study. The pH/surface area dependent metal uptake mechanism (see Section 6.2.4), as well as physical size sorting, seems to control whether the Exchangeable fraction dominates over background Organic Cd levels, both in road runoff and gullypot outflow.

For storm 6B (Figure 6.19 and Figure 6.24(c); see Section 6.3.2), the Organic fraction dominates road runoff speciation. This agrees with the speciation pattern of road dust solids (Figure 6.1) if the Exchangeable fraction is considered to be solubilised by acid rain washing (see 6.2.2.1). Gullypot liquor solids also produce suspended solid Cd, mostly in the Organic fraction, which is observed in the gullypot outflow at the beginning of storm 6B. However, in accord with a pH or redox/surface area dependent suspended solid metal uptake mechanism, as previously described, dissolved Cd is adsorbed to mobilised gullypot sediment during the late stages of storm 6B. This gives rise to a large release of Exchangeable Cd through the gullypot outflow during intense rainfall, in this case greater than 1.5 l/s.

For a smaller storm such as the gullypot outflow of storm 6D (Figure 6.20 and Figure 6.30) Organic Cd dominates the profile, suggesting that the gullypot controls the outflow solid Cd species. The secondary peak corresponds to peak flow and may be due to incoming road runoff.

Suspended Solid Cd  $\mu\text{g}/\text{min}$

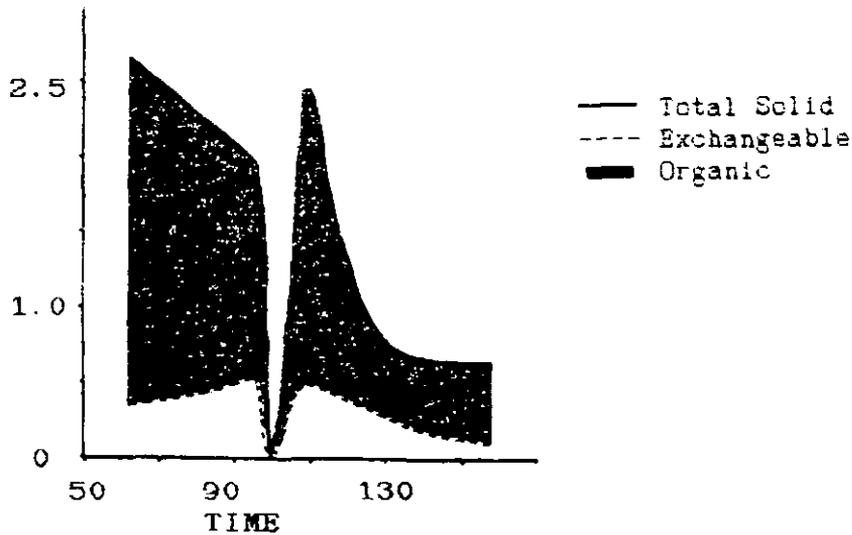


Figure 6.30 Suspended Solid Cadmium Loading Variations for Storm 6D.  
Time in minutes

In storm 6E the first part of the storm is dominated by Organic Cd (Figure 6.31) which suggests that the road runoff dominates the gullypot outflow for suspended solid Cd. The second peak is insignificant and contains a higher proportion of Exchangeable Cd. Considering the evidence from storm 6D this would suggest that mobilised gullypot sediment has increased in importance, compared to road runoff, in the late stage of the storm event.

Total Solid Cd  $\mu\text{g}/\text{min}$

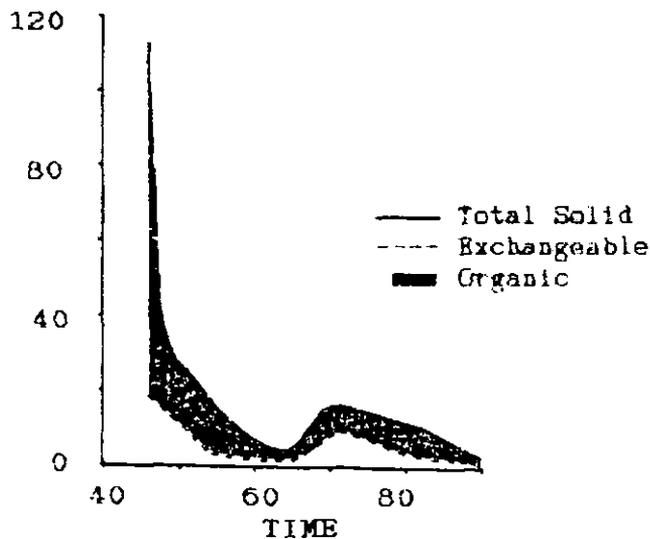


Figure 6.31 Suspended Solid Cadmium Loading Variations for Storm 6E.  
Time in Minutes

6.3.2.7 Suspended Solid Lead Fractions.

The Exchangeable fraction dominates gullypot outflow loadings of suspended solid Pb. However, at the beginning of storm events the Carbonate and Hydrous Metal Oxide Pb fraction may become significant, probably due to the oxidation of reduced interstitial waters.

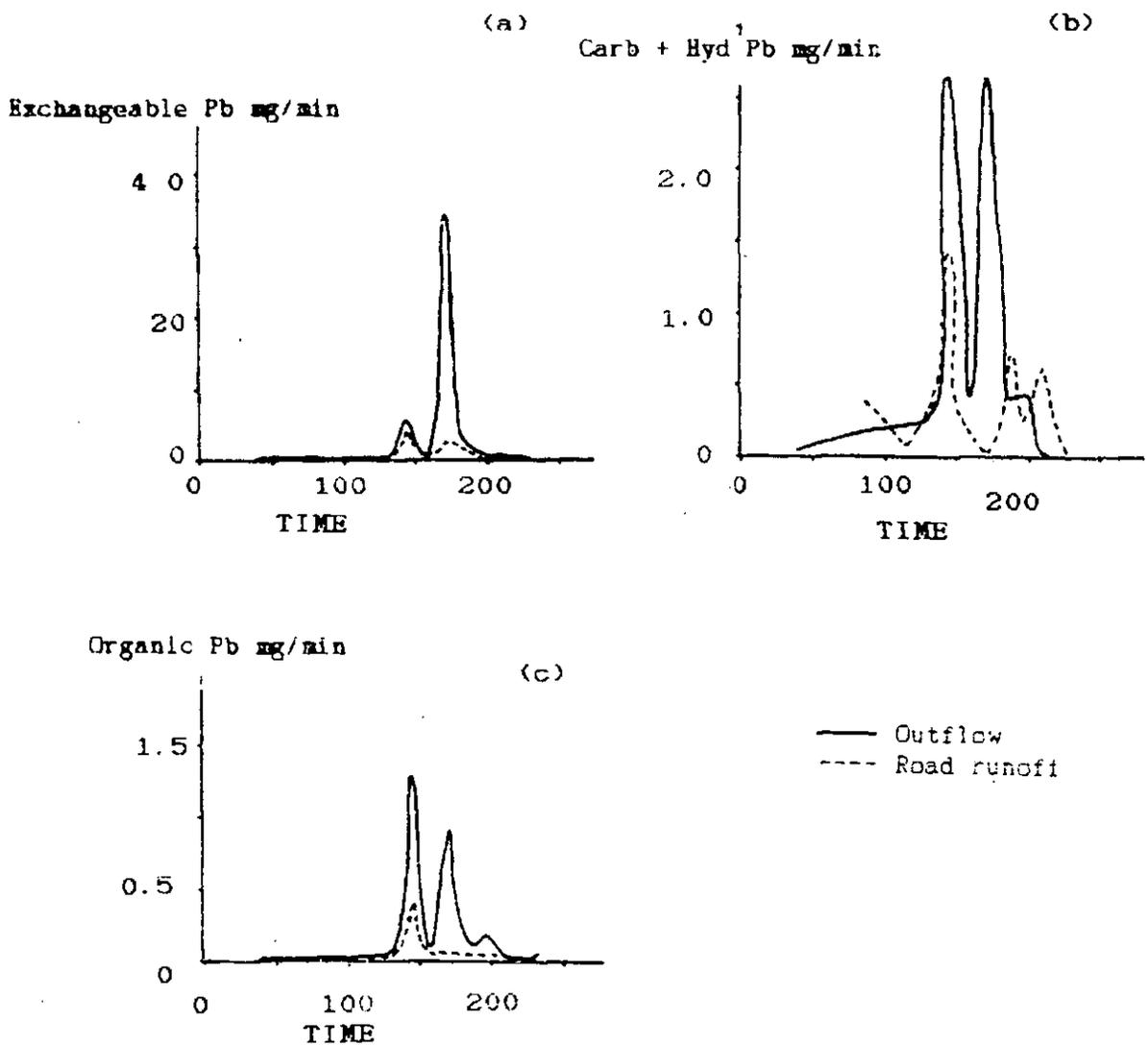


Figure 6.32 Suspended Solid Lead Fractions Loading Variations for Storm 6B.  
Time in Minutes

For storm 6B the suspended solid fractions are shown separately in Figure 6.32(a)-(c). All three show similar loading profiles to suspended solids (Figure 6.19) although with different origins and processes affecting the metal fractions. The Exchangeable Pb fraction (Figure 6.32(a)) dominates over the other fractions through most of the storm and is, for the first pollutant peak, derived from road runoff. The second main peak however is due to mobilised gullypot basal sediment (Figure 6.32(b)), as discussed in Section 6.3.1.1, and is similar to the Cd profile (Figure 6.24). In the same way as for Exchangeable Cd it is suspected that a redox/surface area dependent solid uptake of dissolved Pb is responsible for this peak of gullypot outflow metal. To support this process the Carbonate and Hydrous Metal Oxide fraction increases over road runoff in the outflow (Figure 6.32(b)) which may suggest that the redox change creates new hydrous Fe and Mn oxides in the gullypot which can take up dissolved Pb. Organic Pb (Figure 6.32(c)) is contributed by both road runoff and the gullypot for the first major peak, but only from the gullypot for the second peak.

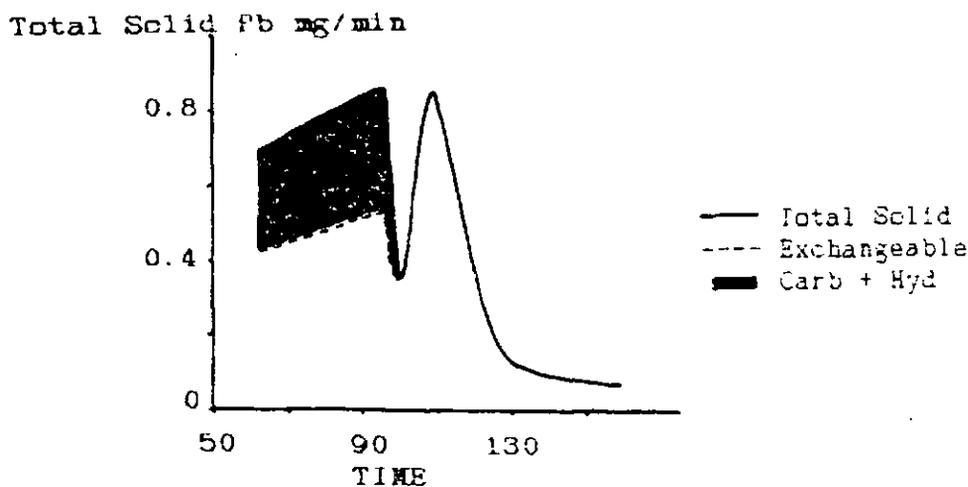


Figure 6.33 Suspended Solid Lead Loading Variations for Storm 6D.  
Time in Minutes

During the low flow storm (6D), Exchangeable Pb dominates the loading profile in the gullypot outflow (Figure 6.33). The first section of the profile contains a large amount of Carbonate and Hydrrous Metal Oxide Pb which may result from the fresh co-precipitation of Hydrrous Fe and Mn oxides in the gullypot liquor. The Fe(III) and Mn(IV) originate from mobilised interstitial sediment water. A secondary peak is also observed which corresponds to an input of solids enriched in Exchangeable Pb from the road surface.

6.3.2.8 Suspended Solid Copper fractions.

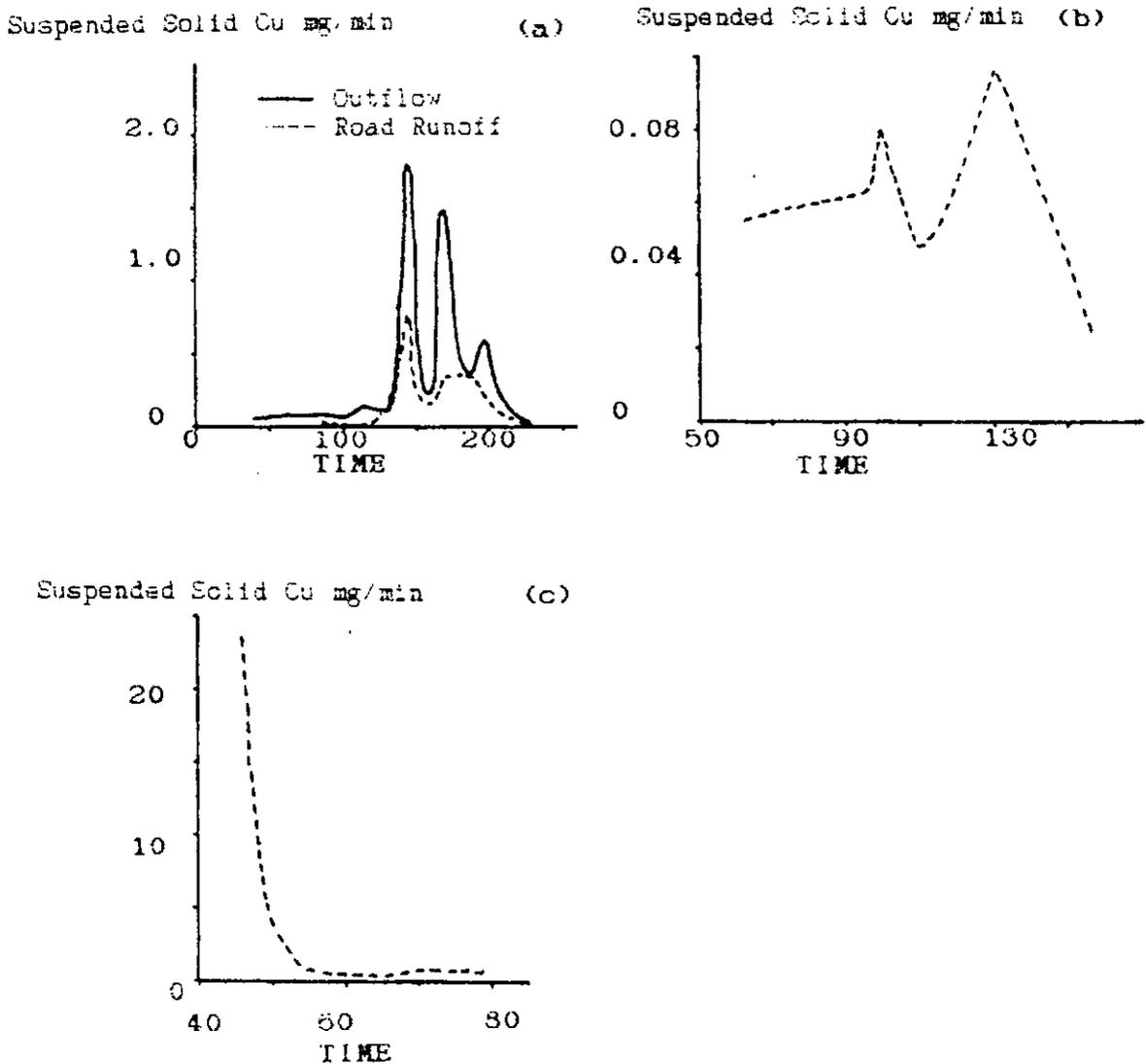


Figure 6.34 Suspended Solid Copper Loading Variations in Gullypot Outflow.  
Time in Minutes

Suspended Solid Cu tends to show a more even distribution over the three solid fractions than the other metals, although the Carbonate and Hydrrous Metal Oxide fraction usually dominates.

The outflow of particulate associated Cu for storm 6B (Figure 6.19 and Figure 6.34(a)) closely follows suspended solids loadings except for a final peak. This final peak is derived from the gullypot and is due to a final flush of fine Cu enriched particles from the gullypot. Road runoff is most important at the beginning of the storm event, but for the second major peak, due to the mobilisation of gullypot solids, the gullypot contributes most of the suspended solid Cu. In a similar way to Zn the Carbonate and Hydrrous Metal Oxide fraction is most important for the gullypot mobilisation peak, suggesting redox/surface area dependent solid Cu uptake for the basal sediments.

During storm 6D (Figure 6.20 and Figure 6.34(b)) most of the profile is due to the Carbonate and Hydrrous Metal Oxide fraction following suspended solid loadings. However, a late Exchangeable Cu peak is observed which may be related to the higher loadings of Cu coming in from road runoff.

Storm 6E (Figure 6.23 and Figure 6.34(c)) shows a significant dilution-exhaustion effect for suspended solid Cu, with a negligible amount mobilised during the second stage of the event.

### 6.3.3 Metal Species Resulting from Different Sources and Processes in the Gullypot System.

The major metal species associated with the dissolved and suspended solid phases, as a direct result of different sources and processes, in the gullypot system are summarised in Table 6.14. Individual metal species, allowing for in-pipe speciation changes, could be used to tentatively fingerprint the mobilisation of different parts of the stormwater system, although in some cases a particular metal fraction may be derived from several sources. It should be stressed that this approach would be most effective at the outfall to a single gullypot

and is increasingly more difficult to apply through the stormwater system. This is mainly the result of different contributions and in-pipe processes.

Table 6.14 Metal Species in Gullypot Outflow Related to Possible Source Inputs.

		Road Runoff		Gullypot		
				Liquor	Interstitial Sediment Water (inferred)	Basal Sediment (inferred)
Zinc	Diss	Chel. Rem.	Str. Bound	Str. Bound		
			Chel. Rem.	Chel. Rem.		
	SS	Exchang.	Carb + Hyd	Carb + Hyd		Exchang.
			Organic			Carb + Hyd
						Organic
Cadmium	Diss	Chel. Rem.	Str. Bound	Str. Bound		
			Chel. Rem.	Chel. Rem.		
	SS	Exchang.	Exchang.	Organic		Exchang.
		Organic	Organic			
Lead	Diss	Chel. Rem.	Str. Bound	Str. Bound		
			Chel. Rem.	Chel. Rem.		
	SS	Exchang.	Exchang.	Carb + Hyd		Exchang.
			Carb + Hyd			
Copper	Diss	Chel. Rem.	Str. Bound	Str. Bound		
			Chel. Rem.			
	SS	Exchang.	Exchang.	Carb + Hyd		Carb + Hyd
		Carb + Hyd	Carb + Hyd			
		Organic	Organic			

Chel. Rem = Chelex Removeable, Str. Bound = Strongly Bound  
 Exchang. = Exchangeable, Carb + Hyd = Carbonate + Hydrous Metal Oxide  
 SS = suspended solids, Diss = dissolved

On the parking lot catchment studied, the dissolved phase road runoff for all four metals was clearly dominated by the Chelex Removeable fraction. This reflects the importance of acid rain mobilisation in releasing metals from road dusts (see Section 6.2.2.1) and thus increasing road runoff metal levels. Some of the dissolved metals are initially complexed by organic compounds giving Strongly Bound metal (see Section 6.2.3) in the road surface runoff, but the Chelex Removeable fraction is considerably more significant. The major Strongly Bound fraction, for all four metals, is produced as a result of mobilised gullypot liquor and interstitial sediment water.

The Exchangeable fraction is important for all four suspended solid associated metals in road runoff (Table 6.14). Although this to some extent reflects the speciation of fine road dust associated metals, a pH/surface area dependent suspended solid metal uptake mechanism (see Section 6.2.4) increases the Exchangeable metal levels in road runoff. In the gullypot the Carbonate and Hydrous Metal Oxide fraction, for all four metals, becomes important due to the fresh precipitation of Fe(III) and Mn(IV) as hydrous oxides or as a result of the contact of incoming oxygenated waters with reduced gullypot liquor and interstitial sediment water. This is therefore a redox/surface area dependent metal uptake process (see Section 6.2.4). Mobilised basal gullypot sediment is dominated by the Exchangeable fraction for Cd and Pb, and by the Carbonate and Hydrous Metal Oxide fraction for Zn and Cu. It may be that although hydrous Fe and Mn oxides represent freshly formed metal uptake sites, Cd and Pb are only weakly associated to the hydrous oxides and therefore are found to be in the Exchangeable fraction.

No information as yet exists on the metal species found for stormwater in-pipe deposits when they are mobilised and washed through the stormwater system. The same process of metal solubilisation by stormwater should affect this sediment, although acid rain washing would be less significant due to the higher pH values found in-pipe compared to on the road surface (due to the buffering of rain water by in-pipe cement dissolution). However, these higher pH values should

lead to an increase in the pH/surface area dependent solid metal uptake process, and therefore higher Exchangeable metal values at the stormwater outfall.

#### 6.4 Heavy Metal Mass Flows through the Gullypot System.

The creation of a mass balance for a particular metal or metal fraction requires the measurement of concentrations and calculation of loadings of the particular metal for individual storm events and for all parts of the gullypot system. This approach was possible on the Chalmers catchment because of the closed and well defined nature of the system, minimising unexpected metal gains or losses; this was the main problem encountered by Malmqvist (1983) when attempting to mass balance metal flows through the Bergsjön catchment. The aim of carrying out a mass balance on the gullypot system was to provide some insight into the extent of the metal mobilisation processes affecting metal species, as discussed in 6.2, as well as to consider the relative persistence of individual metals and metal species.

A representation of the gullypot system under study is given in Figure 6.35, which will also be used to record the mass flows of metals. Atmospheric fallout, road sediments, road runoff, gullypot liquor and gullypot outflow were sampled as described in Chapter 3. It was not possible to sample the gullypot basal sediment, or determine the amount of sediment present, without affecting the experiment. Therefore metals in this part of the system were determined by the subtraction of road runoff and gullypot liquor loadings from gullypot outflow loadings. The most comprehensive range of samples were collected in storm 6B and therefore the data for this storm will be most frequently used to demonstrate metal balances through the gullypot system.

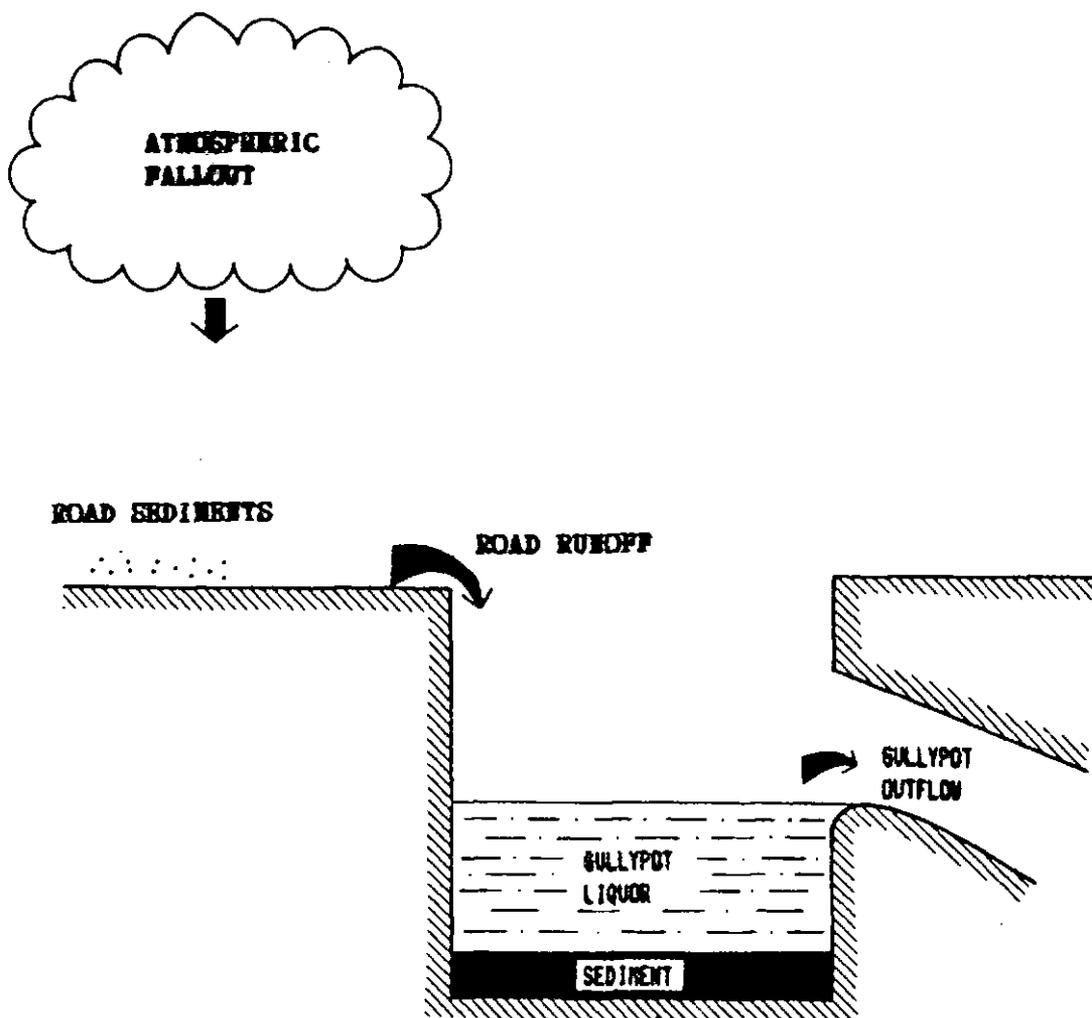


Figure 6.35 Representation of the Gullypot System.

#### 6.4.1 Zinc Mass Balance.

The mass balance for total Zn is shown in Figure 6.36 for storm 6B. The value for road runoff is not included as some Zn contamination in the road runoff was suspected. Rubber tubing was used to transfer samples of road runoff and, although it did not have any contact with other samples, some contamination with Zn may have resulted. Polyethylene tubing was used for all other samples collected.

Atmospheric fallout entering the catchment contributed between 18.1 and 240.1 mg Zn for the storm events sampled. A value of 240.1 mg was recorded in storm 6B, which was the highest measured loading and may be the result of Zn accumulation in the atmosphere over the previous ten dry days. However, no relationship was observed between dry period and Zn loadings in atmospheric fallout. Road dusts may also contribute Zn to road runoff. The available road dust loadings for Zn varied from 518.9 mg to 2427.1 mg during the sampling period, with 2427.1 mg Zn available for washoff during storm 6B.

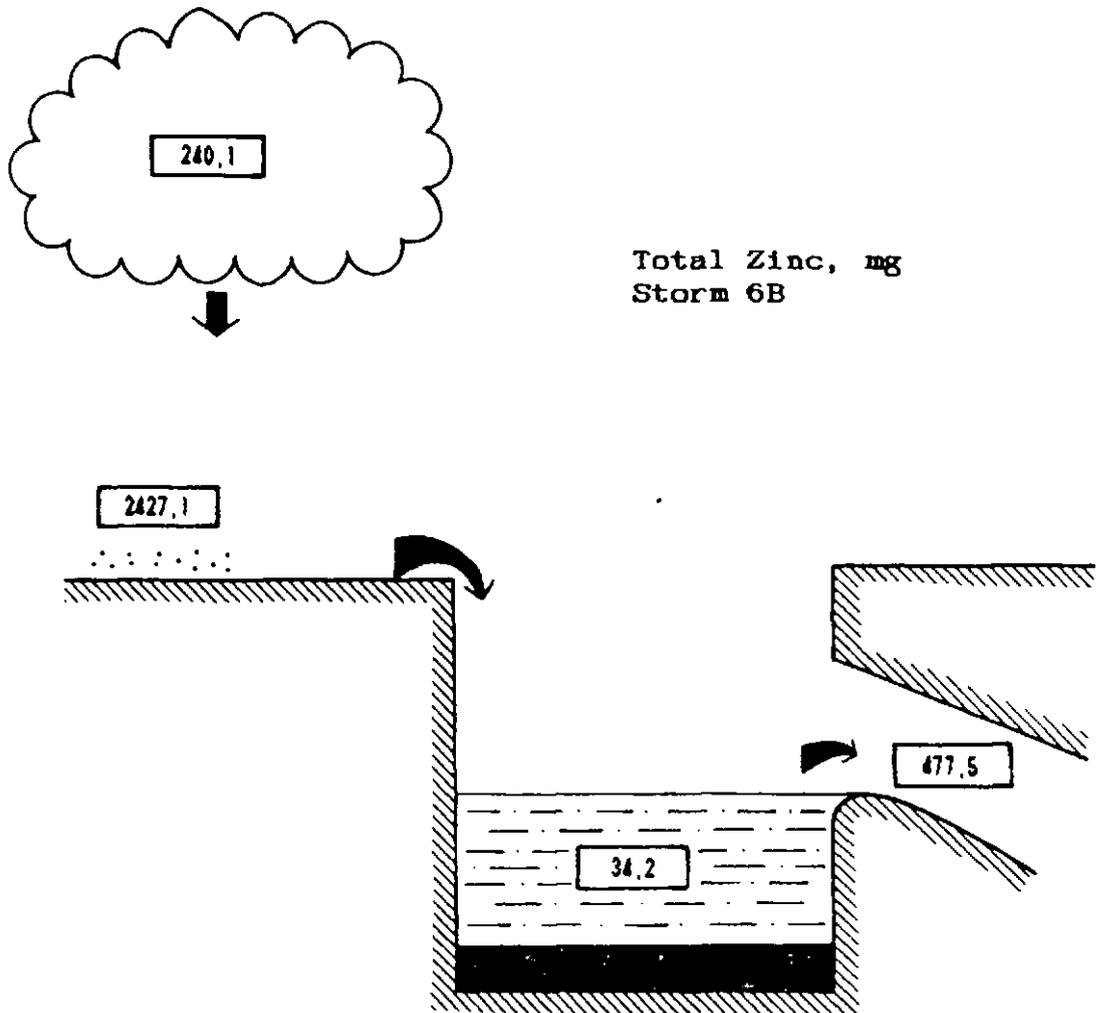


Figure 6.36 Mass Balance for Total Zinc, Storm 6B.

The gullypot liquor loading varied from 1.95 to 34.2 mg of Zn. Storm 6B removed the largest gullypot accumulation of Zn (34.2 mg) which was produced as a result of metal release from the gullypot sediment over a dry period of 10 days. Lower Zn accumulations were observed in later storms due to the heavy flushing of the basal sediment which occurred during storm 6B. Gullypot liquor contributed between 0.7% and 7.2% of Zn in outflow, with 7.2% in storm 6B. The gullypot liquor contribution is most significant during the early stages of the storm event. After 102 minutes of storm 6B the gullypot outflow had released 185.3 mg Zn, which means that at that stage 18.5% of Zn in the outflow had been contributed by gullypot liquor.

The gullypot outflow loadings were between 135 mg and 477.5 mg for each of the storms studied, with 477.5 mg for storm 6B. Road dust accumulation was on average 53.5 mg/day during the sampling period and therefore can account for much of the outflow metal, although atmospheric fallout is also an important Zn source. The outflow Zn loadings reveal no relationship with flow volume; for example the relatively small storm 6C produced 278.2 mg Zn and the larger storm 6F produced only 228.7 mg Zn. This can be explained by the solubility of Zn causing most of the readily released Zn to be washed off early in storm events, in which case it is not storm characteristics but the extent of Zn inputs that determine Zn loadings in gullypot outflow.

#### 6.4.2 Cadmium Mass Balance.

The mass balance of Cd for storm 6B is shown in Figure 6.37. Atmospheric fallout (0.35 mg) is relatively small for this storm, compared to road runoff (1.58 mg). In the storm events studied atmospheric fallout varied between 0.02 and 0.77 mg. The amount of Cd contained in the road dusts was 2.71 mg for storm 6B (range for all storms, 0.46-2.71 mg), and this was generally efficiently mobilised in road runoff. Road runoff removed between 38% and 100% of the combined atmospheric fallout and road dust Cd for the storms studied, which may be attributed to acid rain mobilisation. The Chelex Removeable Cd fraction is a good indicator of this mobilisation process due to the

liberation of free and weakly complexed Cd species from suspended solids by the action of acid rain. Indeed, a comparison of Figures 6.37 and 6.38 shows that, in storm 6B, 72.8% of road runoff transported Cd is in the Chelex Removeable fraction (the average for the sampled period was 80.7%). Another contribution of Chelex Removeable Cd is obtained from the gullypot sediment. This may be due to the acid washing of basal sediment and also the result of the bacterial maturation of the same sediment producing dissolved Cd species.

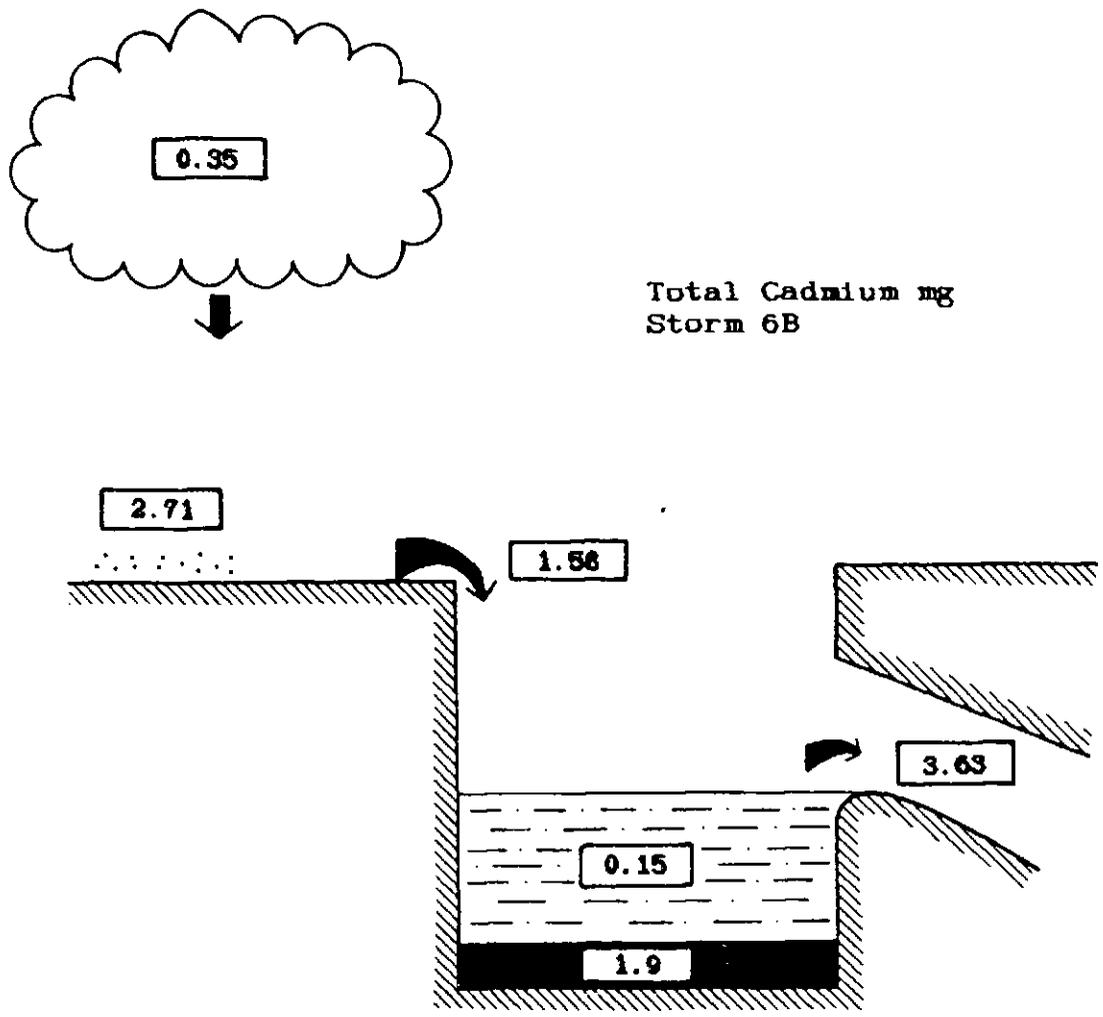


Figure 6.37 Mass Balance for Total Cadmium, Storm 6B.

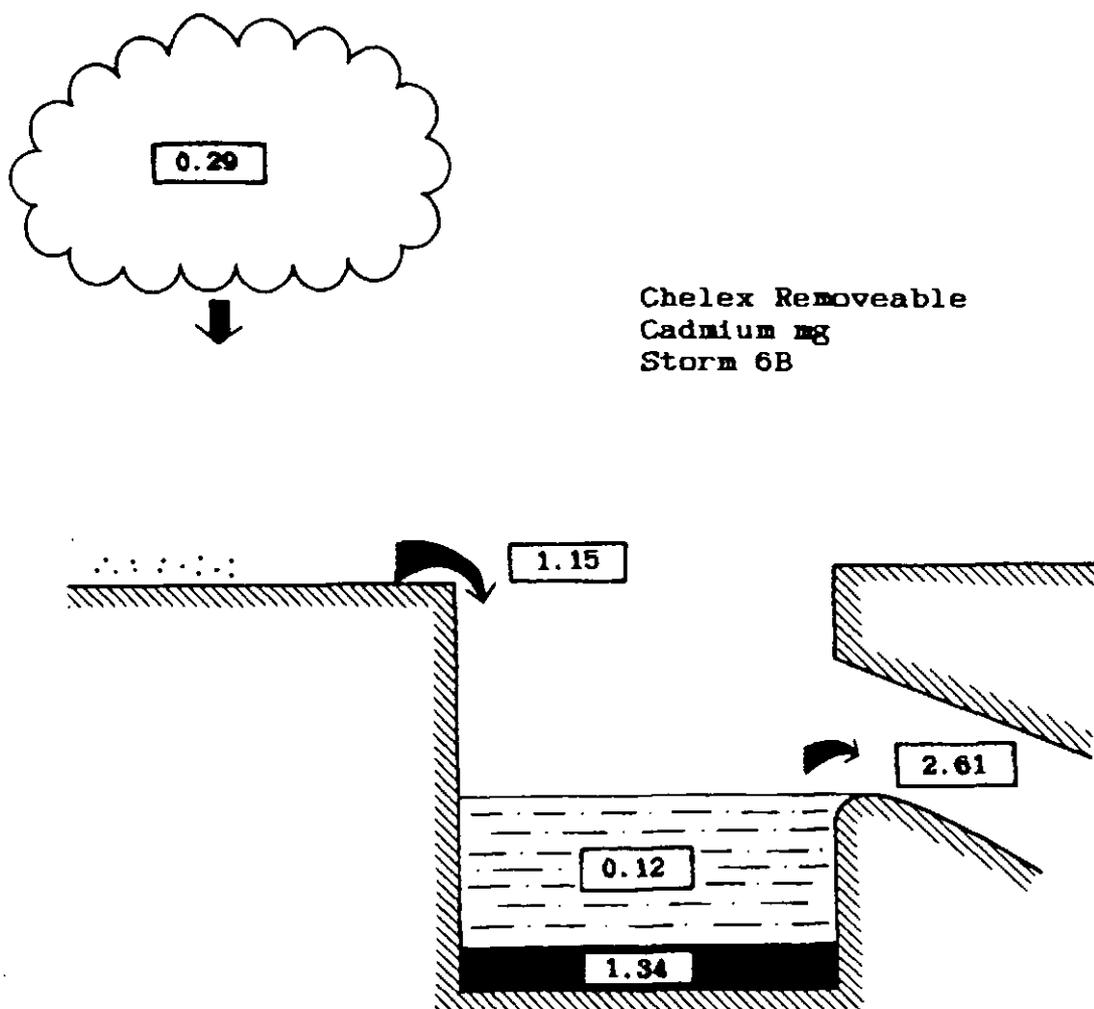


Figure 6.38 Mass Balance for Chelex Removeable Cadmium, Storm 6B.

The gullypot liquor (Figure 6.37) contains 0.15 mg of Cd, representing 4.1% of the gullypot outflow Cd during storm 6B. For all the storms studied, the gullypot liquor content varied from 0.03 mg to 0.15 mg Cd; a contribution of between 0.3% and 5.7% of the gullypot outflow Cd. At the beginning of storm events, Cd in the gullypot can have an important influence on the outflow composition. Figure 6.39 shows that during the first 102 minutes of storm 6B, 2.34 mg of Cd was released through the outflow of which 6.4% was from the gullypot liquor. The gullypot sediment had already released its quota of 1.9 mg of Cd by this time, which is probably due to the corresponding release of

interstitial sediment water. However, only 18.4% of the road runoff Cd had been released and therefore road runoff does not show the same early flush of Cd exhibited by the gullypot. 62.8% of the Cd washed off the road in the remainder of the storm was in the Chelex Removeable fraction which suggests that the acid washing of road sediments is an important contributor to late Cd loading peaks.

Total Cadmium mg

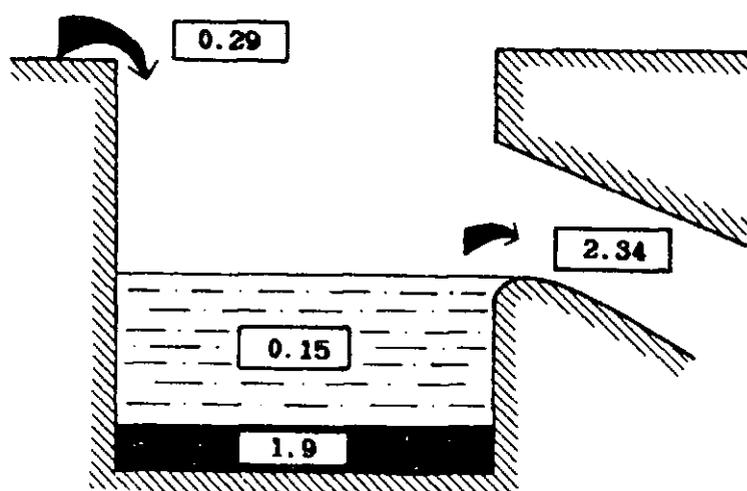


Figure 6.39 Mass Balance for Total Cadmium after 102 Minutes of Storm 6B.

The gullypot sediment had been maturing for ten days prior to storm 6B and the organic maturation products, contained in the interstitial water, had retained significant quantities of Strongly Bound Cd (Figure 6.40). Atmospheric fallout and road runoff contribute a relatively insignificant Strongly Bound Cd fraction as most of the Cd is present in the Chelex Removeable fraction from the acid washing of sediments. Usually the gullypot liquor contributes more significantly to Strongly Bound Cd outflow. However in this case the gullypot liquor had been replaced by road runoff one day previously by a small storm event (128 litres). During the small event 0.26 mg of Strongly Bound Cd was washed out of the gullypot outflow from the gullypot liquor. The contribution of 0.57 mg of Strongly bound Cd from the gullypot interstitial water is obviously the most important source for outflow.

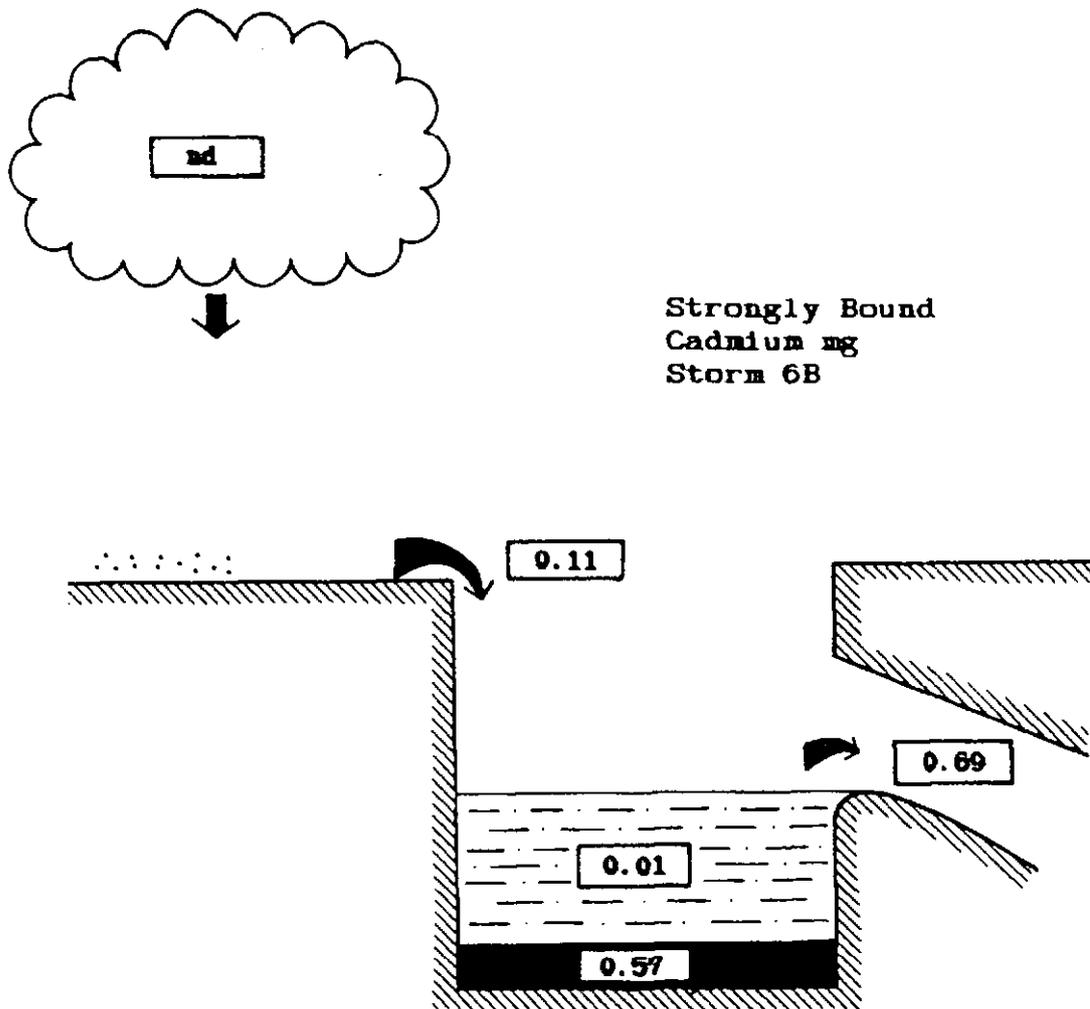


Figure 6.40 Mass Balance for Strongly Bound Cadmium, Storm 6B.

Most of the Cd mobilised in the gullypot system is therefore in dissolved forms as a result of gullypot sediment maturation and the acid rain washing of road sediments. The amount of Cd in the gullypot outflow therefore is not necessarily related to the storm size. With a range of 0.91 mg to 3.63 mg for the sampled storm events, storm 6B was not insignificant with 3.63 mg of Cd (Figure 6.37). The accumulation of Cd in road dusts between storms is on average only 0.062 mg/day and therefore atmospheric fallout and even the removal of Cd from the road surface itself must contribute significantly to the outflow. It is

clear, though, from Figure 6.37 that Cd is not a persistent metal and is almost completely mobilised during each storm event.

#### 6.4.3 Lead Mass Balance.

Atmospheric fallout of Pb is important for storm 6B with a contribution of 203.0 mg (Figure 6.41). The input is probably the Pb aerosols and fine dusts, from vehicular emissions, suspended in the atmosphere. This Pb source is variable and was in the range 31.7-361.8 mg Pb for the sampled storms.

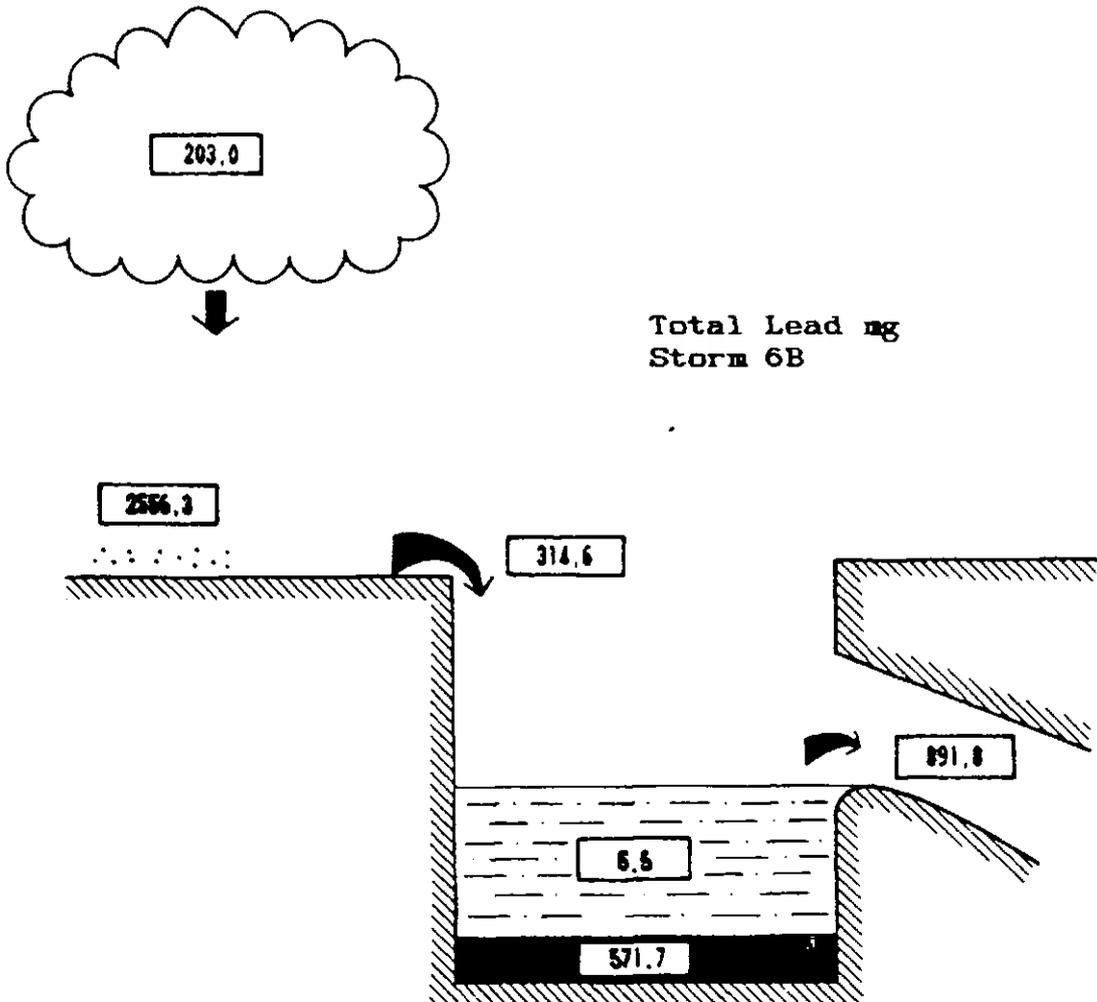


Figure 6.41 Mass Balance for Total Lead, Storm 6B.

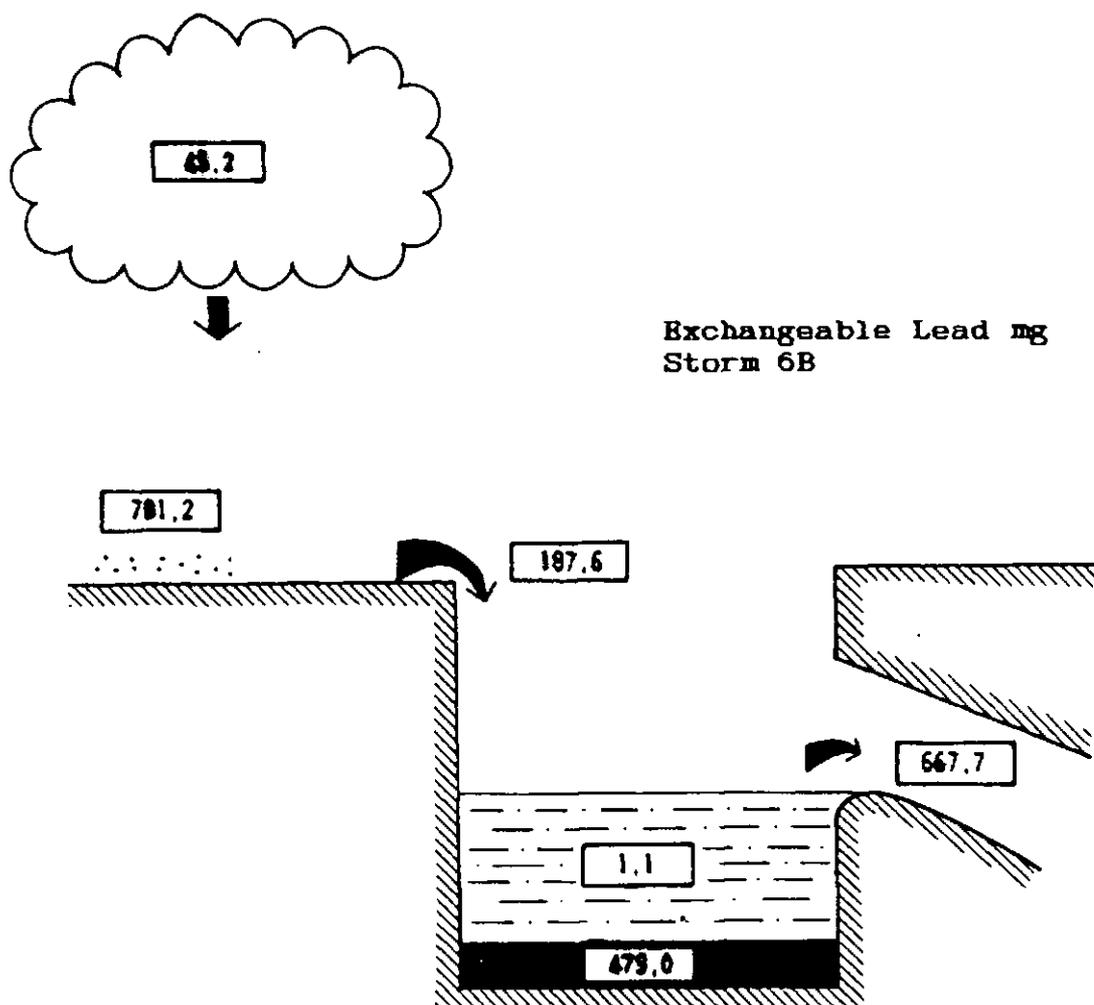


Figure 6.42 Mass balance for Exchangeable Lead, Storm 6B.

Road dusts contained a loading of between 545.8 and 2556.3 mg Pb, with the highest value in storm 6B. Between 4.5% and 11.4% of the Pb contained in combined atmospheric fallout and road sediments are washed off in road runoff. The extent of the acid rain washing of Pb from sediments is less than for Cd with an average of only 13.2% of Pb in the Chelex Removeable fraction (8.6% for storm 6B). As shown for storm 6B in Figure 6.4.2, the Exchangeable fraction in road runoff represents 22.7% of the combined atmospheric fallout and road dust source. The Exchangeable fraction represents 82.2% of the total solid

Pb washed off, yet is only 30.6% of the total Pb in road dusts. This may be due to the action of the pH/surface area dependent suspended solid uptake process resulting in the adsorption of dissolved Pb, which has been released from road sediments, onto suspended solids. A similar Exchangeable enrichment process, involving both pH and redox changes, may also result in the increased outflow loading resulting from gullypot basal sediment (see Section 6.2.4).

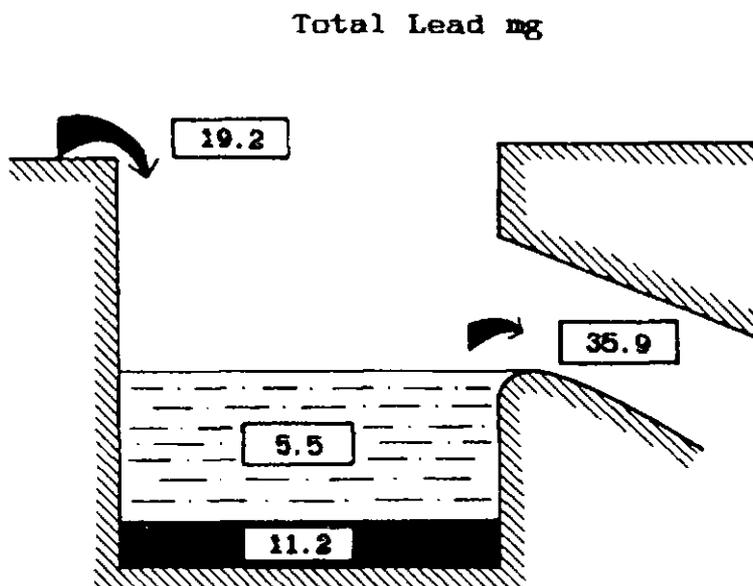


Figure 6.43 Mass Balance for Total Lead after 102 Minutes of Storm 6B.

The gullypot liquor contained 5.5 mg Pb in storm 6B (Figure 6.41) which represented only 0.6% of the Pb in gullypot outflow. For all storm events studied the gullypot liquor produced between 0.16 and 5.5 mg Pb, which represented between 0.17% and 2.66% of outflow Pb. The percentage contribution tends to be greater in small storms, although the amount of gullypot liquor Pb accumulation is also important. During the early stages of storm 6B the gullypot liquor contributed 15.3% of the Pb in the outflow (Figure 6.43). Lead is also less easily solubilised than Cd and only 2% of the potentially available Pb in the basal sediment has been mobilised after 102 minutes. Therefore the higher flow in the late stages of storm 6B were

required to mobilise the gullypot basal sediment Pb, as well as the remaining 295.4 mg of road runoff. The 11.2 mg Pb which had been mobilised in the gullypot sediment probably represents the Pb contained in interstitial sediment water.

The gullypot outflow of Pb, therefore, is very dependent on whether the gullypot sediment is mobilised and on the suspended solid Pb loadings in road runoff. However, approximately 90% of the road dust Pb remains on the road surface and it is therefore a relatively persistent metal. The gullypot outflow loading for storm 6B was high (891.8 mg) largely due to gullypot sediment mobilisation (Figure 6.41). The gullypot outflow released between 75.7 mg and 891.8 mg Pb in the sampled storms, and correlated well with loadings of suspended solids and particulate organic carbon. The average accumulation rate in road dusts was 56.2 mg Pb/day between storms which is sufficient to meet the outflow loadings found, although atmospheric fallout is also important.

#### 6.4.4 Copper Mass Balance.

The atmospheric fallout loadings of Cu (ranging between 2.0 and 203.4 mg Cu) are frequently greater than gullypot outflow loadings for the sampled events. During storm 6B, 203.4 mg Cu was contributed by atmospheric fallout (Figure 6.44).

As in the case of Pb, a large reservoir of Cu is present in road dusts, yet only between 5.3% and 9.8% of Cu in combined road dusts and atmospheric fallout is washed off in road runoff. The loading of Cu in road dusts was in the range of 148.6 mg - 3465.8 mg Cu. However, acid washing of sediments appears to be a fairly important Cu removal process, as an average of 49.8% of the Cu in road runoff (for all the storms studied) is in the Chelex Removeable fraction.

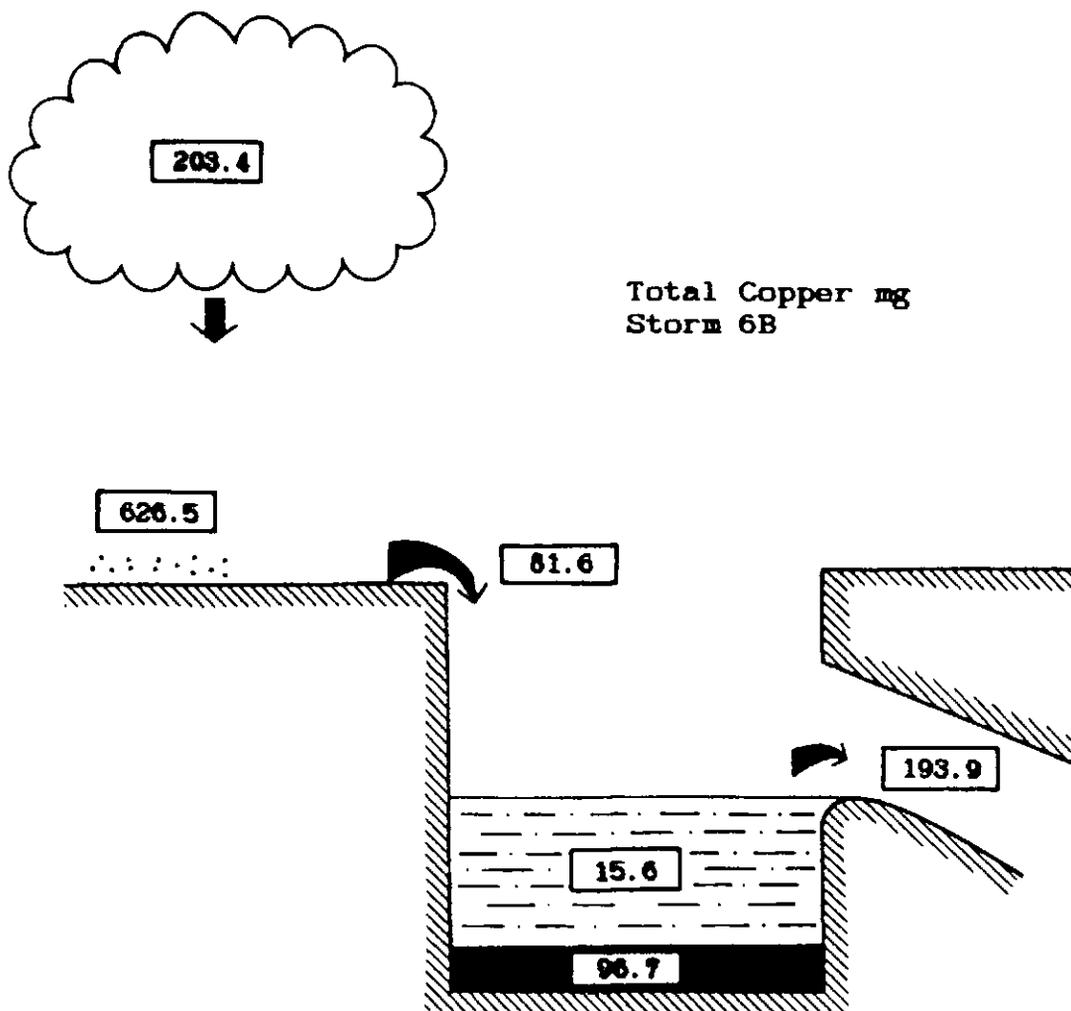


Figure 6.44 Mass Balance for Total Copper, Storm 6B.

The gullypot liquor is an important source of Cu and produced 15.6 mg of Cu for storm 6B, which represented 8% of the gullypot outflow. During the sampling period the gullypot liquor contained between 3.1 and 15.6 mg Cu which represented contributions of between 3.7% and 12.3% of the gullypot outflow Cu loading. As was found for the other metals the gullypot liquor is most important during the early stages of a storm event. During storm 6B, the gullypot liquor contributed 18.6% of the Cu after 102 minutes (Figure 6.45), Copper behaves somewhere in between the extremes of Cd and Pb in that 63.7% of the gullypot basal sedimentary Cu was released in the first part of storm

6B. This represents Cu in interstitial sediment waters with a further 35.1 mg Cu still bound to sediment and to be released later in storm 6B. Only 8.3% of the road runoff Cu had been released by 102 minutes, with the remainder coming in later from road sediment mobilisation and the acid rain washing of sediments.

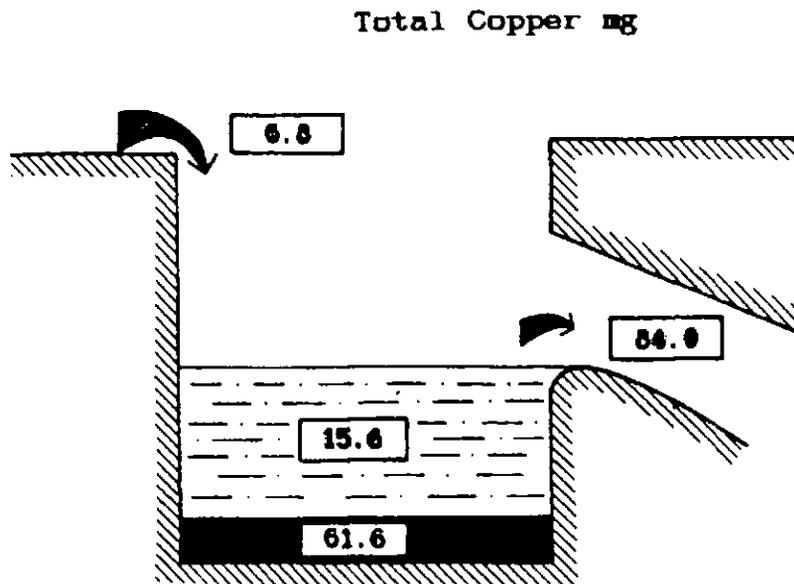


Figure 6.45 Mass Balance for Copper after 102 Minutes of Storm 6B.

The gullypot interstitial sediment water can be an important source of the Strongly Bound Cu fraction (Figure 6.46). In storm 6D, 98% of the Strongly Bound Cu in outflow came from interstitial sediment water, with the remainder from road runoff and none from atmospheric fallout. As this fraction was 17.2% of total Cu in the gullypot outflow then the Strongly Bound fraction in interstitial sediment water is a significant source of Cu. This fraction results from the complexing of Cu with matured sediment derived organic compounds.

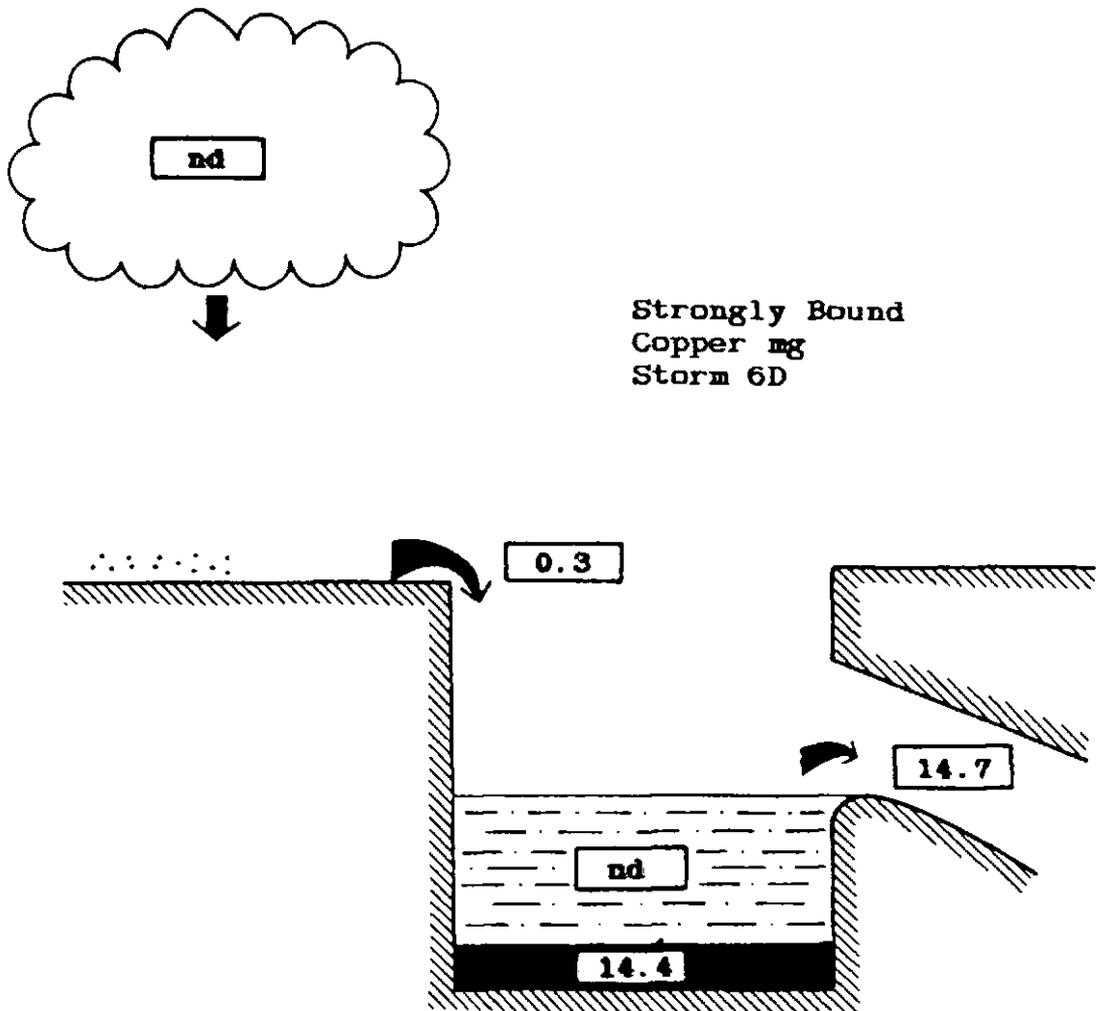


Figure 6.46 Mass Balance for Strongly Bound Copper, Storm 6D.

The gullypot outflow therefore depends both on sediment mobilisation and acid rain mobilisation. During storm 6B (Figure 6.44) 193.9 mg of Cu was released, although a range of 31.8 mg - 193.9 mg Cu was found for the storms studied. This seems reasonable as the average road dust accumulation was 18.7 mg Cu/day.

## CHAPTER 7 METAL SPECIATION IN STORMWATER AND SNOWMELT RUNOFF; CONCENTRATIONS, LOADINGS AND BIOAVAILABILITY.

The occurrence of heavy metals in stormwater in unacceptably high concentrations is a particular cause for concern as they may have a serious impact on sensitive receiving waters (Randall et al. 1978, Wilber and Hunter 1979, Malmqvist 1983).

In order to assess the degree of pollution due to metals in urban runoff it is essential to understand the variations, both in terms of concentrations and loadings, of bioavailable metal species. It is also necessary to analyse the data obtained for violations of Water Quality Standards. Exceedance of these standards may indicate short term effects on the biota of receiving waters. However, the pin-pointing of violations is not aided by the intermittent nature of urban runoff discharge. There is therefore a requirement for analytical methods which can monitor the long term uptake of heavy metal species by receiving water organisms and their reaction, if any, to short term metal polluted stormwater discharges. *Dialysis with Receiving Resins* may provide such an analytical method.

### 7.1 Storm Characteristics.

Eight storm events (four at Oxhey and four at Bergsjön) and two snowmelt events (both at Bergsjön) were investigated for heavy metal species concentrations and loadings. The main characteristics of each storm event are shown in Table 7.1. In addition to analysing the samples for heavy metal species, controlling parameters, such as suspended solids, particulate organic carbon, pH, dissolved chloride and dissolved organic carbon, were also measured.

Table 7.1 Characteristics of Ten Urban Runoff Events Sampled at Stormwater Outfalls in Sweden and the U.K.

Storm Code	Date	Catchment	Samples Collected (No.)	Type of Event	Storm Duration (hours)	Urban Runoff (m <sup>3</sup> )
7A	26.02.83	Oxhey	9	Stormwater	2.2	1058.3
7B	28.02.83	Oxhey	10	Stormwater	2.7	1362.3
7C	28.05.83	Oxhey	5	Stormwater	0.8	320.3
7D	04.05.84	Oxhey	3	Stormwater	nm	nm
7E	04.10.83	Bergsjön	5	Stormwater	0.7	33.4
7F	27.10.83	Bergsjön	12	Stormwater	1.7	63.1
7G	19.09.84	Bergsjön	3	Stormwater	0.4	79.9
7H	18.10.84	Bergsjön	11	Stormwater	4.4	281.3
7I	20.12.83	Bergsjön	12	Snowmelt	6.6	111.7
7J	29.01.85	Bergsjön	12	Snowmelt	9.0	77.1

nm = not measured

Storms 7A and 7B represent a rainy spell at the Oxhey site with a break of 2.7 days separating the two events. The weather for the preceding two months contained isolated snowfalls, and urban salting during this time is reflected in the elevated dissolved chloride concentrations in storm 7A (up to 179 mg Cl/l). The maximum flow intensity was highest in storm 7A, up to 231 l/s, which represents 4.7 l/s/impervious hectare (although it may not have rained over the whole catchment). The highest rainfall intensity sampled at Bergsjön was 82.3 l/s in storm 7G, which represents 13.5 l/s/impervious hectare. Clearly these are not large storms, in comparison with the maximum intensity range of 5.9 to 118 l/s/impervious hectare for the six storms sampled on the Chalmers catchment during the summer of 1984 (Chapter 6). However, storms 7A - 7H were all monitored during spring and autumn and therefore do not represent the heavy thunderstorm events found in the summer. Also the Oxhey and Bergsjön catchments are

not small confined areas and different spatial rainfall intensity and duration may be found in each contributing area. Consequently a high rainfall intensity in one area may be reduced in the subsequent stormwater outflow by a low intensity in another area.

Storms 7E, 7F, 7G and 7H were collected during the autumn seasons of 1983 and 1984 on the Bergsjön catchment (Table 7.1). These four events are typical of the frequent low to medium intensity rainfall events recorded throughout the year in Gothenburg.

Snowmelt events 7I and 7J were collected during the winters of 1984 and 1985 respectively (Table 7.1) and the two events are quite different in character. Snowmelt 7I was collected in December when snow often melts rapidly, either due to the snowfall changing to sleet or rain, or during the frequent warm spells. For 7I the snow had lain on the ground for several days and the first sample was collected as a warm spell had started to melt the snow. After five bottles had been collected rainfall increased the snowmelt process, and consequently the runoff, resulting in a heavy flush of suspended solids (up to 1624 mg/l) and dissolved chloride (up to 17 g/l). In contrast snowmelt 7J was collected during mid-winter (January/February) when ambient temperatures are frequently as low as -20°C. Under these conditions the snow melts over a long time period as a result of road salting and the heat of the sun during daytime. Snowmelt 7J represents only nine hours from these winter conditions, which prevailed from early January to the end of April in the winter of 1985.

#### 7.1.1 Dissolved and Suspended Solid Metal Concentrations.

The average dissolved metal concentrations for all the storm and snowmelt events studied are shown in Table 7.2.

Table 7.2 Average Dissolved Metal Concentrations in Stormwater and Snowmelt.

	Dissolved Metal Concentration $\mu\text{g/l}$									
	7A*	7B*	7C*	7D*	7E*	7F*	7G*	7H*	7I*	7J*
Zinc	227.4	162.8	92.0	158.4	202.3	88.1	65.4	68.7	339.5	508.5
Cadmium	3.4	9.1	2.7	1.7	2.9	1.4	0.6	1.0	6.1	4.3
Lead	17.0	17.8	15.5	16.4	9.0	5.2	3.8	4.0	37.0	8.6
Copper	53.8	47.2	23.5	37.9	138.2	33.6	45.1	68.5	89.2	996.3

\*Stormwater, Oxhey

\*Stormwater, Bergsjön

\*Snowmelt, Bergsjön

In stormwater the dissolved Zn and Cu concentrations are similar for both catchments, whereas the dissolved Cd and Pb concentrations are generally slightly higher in the U.K. catchment. The two snowmelt events at Bergsjön show elevated dissolved concentrations for all four metals compared to the four stormwater events monitored at the same catchment. This has been observed previously for total metal concentrations at Bergsjön (Malmqvist 1983) and has been attributed to the slow melting of metal enriched, dirt-laden snow which collects at the road side.

The greatest snowmelt dissolved metal enrichment is seen for free and weakly complexed (Electrochemically Available and Chelex Removeable) metal species, which is illustrated in Table 7.3 by a comparison of dissolved Cd in stormwater and snowmelt. The same enrichment pattern is observed for Cu, Pb and Zn and can be accounted for by the high dissolved chloride concentration (1-17 g/l) in snowmelt which assists the desorption of weakly associated metal species from suspended solids. On liberation the metal chloride species tend to enter free and weakly complexed fractions. The enrichment factor for all four metals was between 3.6x and 15x for the Electrochemically Available

and Chelex Removeable fractions in snowmelt over stormwater at Bergsjön. The presence of dissolved organic complexing ligands may compete favourably with chloride for the liberated metal. An enrichment of between 1.9x and 5.8x, for all four metals, was found for the Strongly Bound fraction of snowmelt at Bergsjön.

Table 7.3 Average Dissolved Concentrations for Cadmium Fractions in Stormwater and Snowmelt, Bergsjön.

	Dissolved Cadmium Concentration $\mu\text{g/l}$					
	7E*	7F*	7G*	7H*	7I*	7J*
Electrochemically						
Available	2.7	0.7	nd	0.3	4.8	2.4
Chelex						
Removeable	2.3	1.0	0.4	0.8	4.2	3.8
Strongly						
Bound	0.6	0.4	0.2	0.3	2.1	0.5

\*Stormwater, Bergsjön

\*Snowmelt, Bergsjön

nd = not detected

Zinc, Cd and Pb suspended solid concentrations are similar on both the Oxhey and Bergsjön catchments (Table 7.4). The road surface dusts are probably the main source of these three metals on both catchments, as evidenced from the mass balance of the Chalmers parking lot (Chapter 6) and the mass balance of Malmqvist (1983) for the Bergsjön catchment. The metal inputs to both the Swedish and U.K. catchments may be largely attributed to domestic traffic and therefore the accumulation of metals in the road dusts may be expected to be similar. Copper is greatly enriched at the Bergsjön outfall, compared to Oxhey. This can be directly related to the Cu guttering which is widely used within the Swedish catchment, as the road dust concentrations are not particularly high (Table 7.5).

Table 7.4 Average Suspended Solid Metal Concentrations in Stormwater and Snowmelt.

Suspended Solid Metal Concentration $\mu\text{g/g}$										
	7A*	78*	7C*	7D*	7E*	7F*	7G*	7H*	7I*	7I*
Zinc	413,9	551,7	769,8	345,5	272,2	944,8	1211,9	1312,3	663,7	2372,2
Cadmium	11,5	60,3	9,1	3,0	5,1	11,2	6,3	4,7	3,4	11,8
Lead	2464,5	2001,4	939,2	514,0	410,5	663,2	1416,2	1889,8	550,7	4290,4
Copper	413,6	481,5	167,3	126,1	756,0	1043,8	2309,0	3364,3	3071,1	25184,7

\*Stormwater, Oxhey

\*Stormwater, Bergsjön

\*Snowmelt, Bergsjön

The suspended solid metal concentrations at the Bergsjön stormwater outfall are greater than those associated with the fine fraction of road dusts (Table 7.5). This enrichment can be explained for Zn, Cd and Pb by the pH/surface area dependent metal uptake theory, described in Section 6.2.4, with the increase of suspended solid metal being related to the increase in pH from the acidic rainfall ( $\approx 4.0$  at Bergsjön) to the stormwater outfall ( $\approx 6 - 7$  at Bergsjön). This pH increase is believed to be a carbonate process due to the dissolution of road and in-pipe sediment salts, as well as the products of the destruction of concrete pipes. This pH gradient through the stormwater system causes solubilised metal species to adsorb to particulate surfaces, which are  $\approx 20\%$  organic carbon at the stormwater outfall and therefore provide increased complexing sites for the metals. The major metal enrichment of stormwater over road dusts for Zn, Cd and Pb is found in the Exchangeable fraction, as a comparison of Tables 7.5 and 7.6 shows for Pb. The Exchangeable Pb fraction is enriched by between  $13\times$  and  $96\times$  in stormwater solids over the fine fraction of road dusts.

Table 7.5 Average Metal Concentrations (Three Samples) in the Fine Fraction of Road Dusts from the Bergsjön Catchment.

	Metal Concentration $\mu\text{g/g}$			
	Exchangeable	Carbonate and Hydrous Metal Oxide	Organic	Total Solid
Zinc	20.4	138.2	62.0	220.6
Cadmium	1.3	nd	nd	1.3
Lead	27.3	156.8	29.6	213.7
Copper	7.0	45.6	43.7	96.3

nd = not detected

The same Exchangeable enrichment process also occurs for Cu at Bergsjön. However, in mass balance terms most of the Cu is derived from roofing materials (Malmqvist 1983) and this runoff is routed into the stormwater system below ground. The acid rain mobilisation, described in Section 6.2.2.1, would be expected to mostly release Cu in the Chelex Removeable fraction. On contact with the pH buffered, road and gullypot washout the free and weakly complexed Cu may be rapidly adsorbed to the surface of suspended solids. Therefore the pH/surface area uptake process may be only an in-pipe process for Cu.

Table 7.6 Average Suspended Solid Concentrations for Pb Fractions in Stormwater and Snowmelt, Bergsjön.

	Suspended Solid Lead Concentration µg/g					
	7E*	7F*	7G*	7H*	7I*	7J*
Exchangeable	363.6	533.6	834.5	1307.0	363.1	2633.0
Carb + Hyd	39.4	120.5	532.5	532.3	97.3	1428.9
Organic	7.6	9.1	49.2	50.4	90.4	228.6

Carb + Hyd = Carbonate + Hydrous Metal Oxide

\*Stormwater, Bergsjön

\*Snowmelt, Bergsjön

#### 7.1.2 Dissolved and Suspended Solid Metal Loadings.

The dissolved metal loadings for Oxhey and Bergsjön are shown in Table 7.7. It is clear that the metal loadings at Oxhey are much greater than Bergsjön. However, when the eight times greater catchment area of Oxhey is taken into account then the respective site loadings are within the same order of magnitude for the four dissolved metals.

Table 7.7 Dissolved Metal Loadings in Stormwater and Snowmelt.

	Dissolved Metal Loadings, g								
	7A*	7B*	7C*	7E*	7F*	7G*	7H*	7I*	7J*
Zinc	217.7	218.1	28.4	6.3	5.1	4.3	18.8	34.6	37.1
Cadmium	3.0	12.4	1.0	0.07	0.08	0.04	0.25	0.64	0.32
Lead	16.7	24.3	5.4	0.25	0.32	0.31	1.01	6.2	0.67
Copper	52.7	62.7	7.1	3.6	1.9	2.4	17.6	8.9	76.4

\*Stormwater, Oxhey

\*Stormwater, Bergsjön

\*Snowmelt, Bergsjön

Snowmelt clearly has increased dissolved metal loadings compared to stormwater runoff at the Bergsjön site (Table 7.7), particularly for Cd and Cu and to a lesser extent for Zn and Pb, despite a similar total flow runoff volume (Table 7.1).

Table 7.8 Suspended Solid Metal Loadings in Stormwater and Snowmelt.

Suspended Solid Metal Loadings, g									
	7A*	7B*	7C*	7E*	7F*	7G*	7H*	7I*	7J*
Zinc	74.6	38.5	31.8	1.4	3.8	7.9	12.8	13.0	4.7
Cadmium	1.4	3.9	0.4	0.02	0.04	0.03	0.04	0.04	0.02
Lead	371.8	146.6	43.9	1.5	2.9	5.4	18.3	6.4	7.9
Copper	64.1	36.2	8.6	2.2	3.8	12.6	30.8	23.5	42.3

\*Stormwater, Oxhey

\*Stormwater, Bergsjön

\*Snowmelt, Bergsjön

A similar comparison can be made between Oxhey and Bergsjön for the suspended solid metal loadings (Table 7.8). One significant difference is that snowmelt metal loadings are not significantly different from stormwater metal loadings at the Bergsjön site.

If, during snowmelt, an interaction between dissolved and suspended solid loadings occurred in-pipe then, taking into account the significant dissolved metal snowmelt increase (Table 7.7), the snowmelt suspended solid metal loadings would be expected to have decreased accordingly. As this is not the case then it could be suggested that the significant dissolved metal solubilisation is taking place on the road surface during snowmelt.

### 7.1.3 Partitioning of Metals between the Phases and Fractions.

The percentage contribution of each metal fraction to the urban runoff events which have been studied are shown in Figure 7.1. The proportioning of the metal fractions is fairly comparable both between individual storm events and between different catchments.

Zinc shows a presence in both the dissolved and suspended solid phases but, except in storms 7C and 7G, is most important in the soluble form. Free and weakly complexed Zn predominate in stormwater with an average of 40.6% in the Electrochemically Available fraction and 45.4% in the Chelex Removeable fraction. These fractions, particularly the Electrochemically Available fraction (73.5%), are increased significantly in snowmelt runoff. This tends to confirm the formation of soluble chloride complexes of Zn during appropriate conditions. Apart from storms 7A and 7E where the Strongly Bound Zn fraction is considerably elevated, the Strongly Bound fraction remains consistent at 15.8% and 15.9% for the Oxhey and Bergsjön catchments respectively, increasing only slightly in snowmelt runoff. The elevated Strongly Bound fractions in storms 7A and 7E may be due to the importance of dissolved organic complexing compounds from gullypot liquor and interstitial sediment water (see Section 6.3.3). In the suspended solid phase the Exchangeable fraction is the most important, accounting for, on average, 22.3% of the total Zn in stormwater collected from both catchments. However, there is considerable variation in Exchangeable Zn between storms. As Exchangeable Zn is mostly derived from road runoff solids and gullypot basal sediments (see Section 6.3.3), the mobilisation of these solids and the extent of the pH/surface area dependent metal uptake process (see Section 6.2.4) is critical for the importance of this fraction. The more strongly associated sedimentary Zn fractions also show variable tendencies. The Carbonate and Hydrrous Metal Oxide fraction is significant for stormwater at Bergsjön (12.5%), while the Organic fraction is more important at Oxhey (11.1%) and for snowmelt at Bergsjön (14.5%).

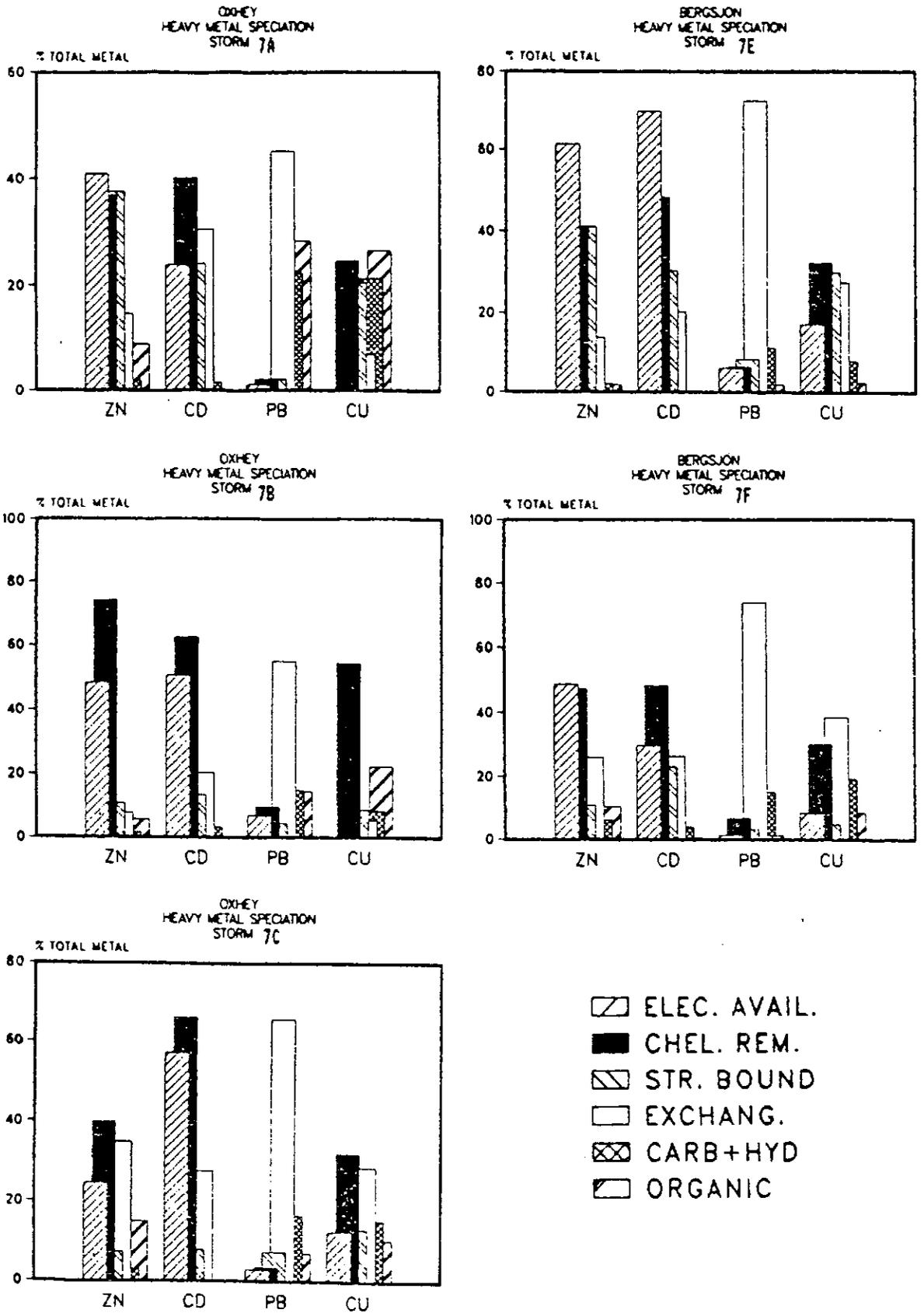


Figure 7.1 Partitioning of Metals between Fractions in Urban Runoff.

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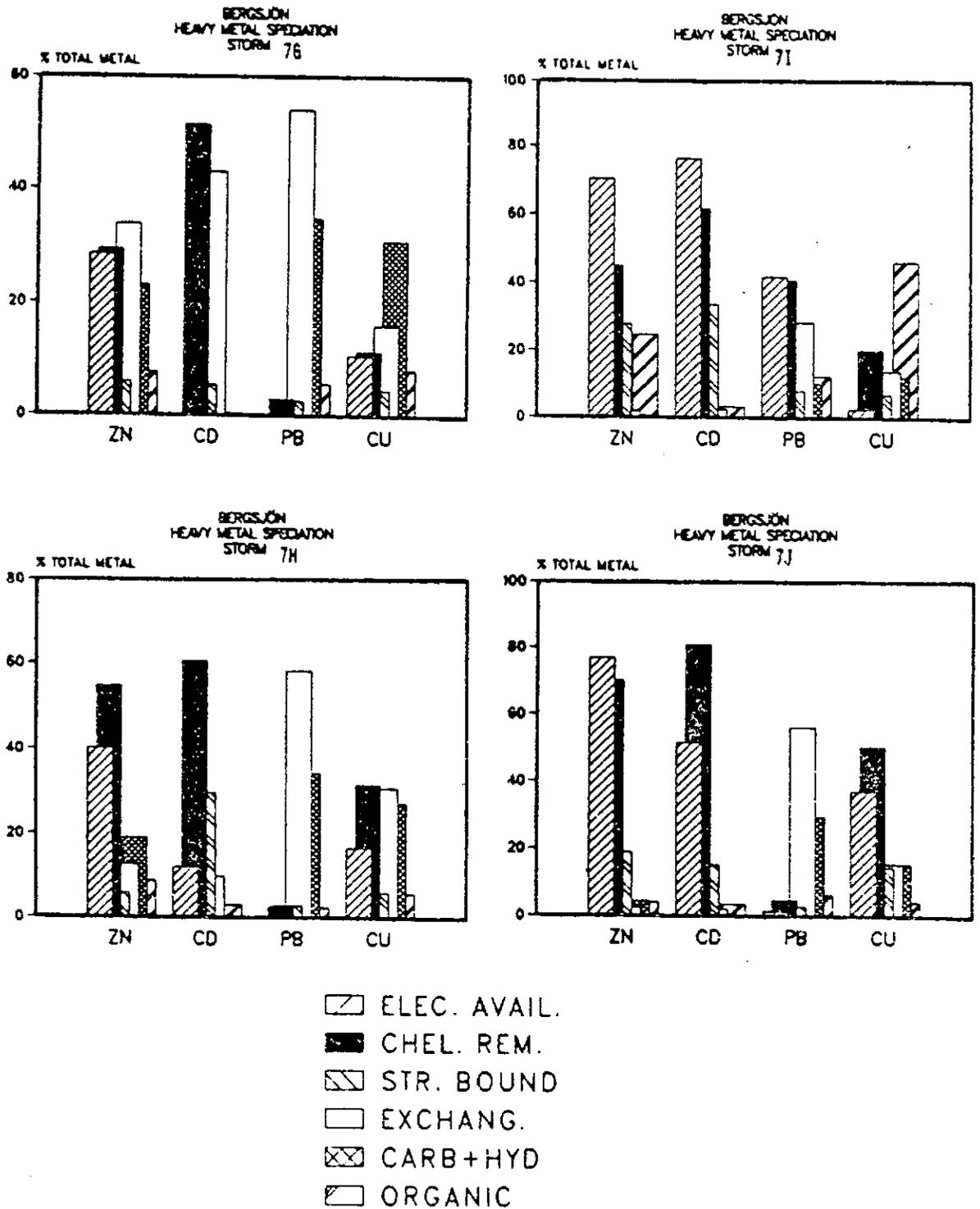


Figure 7.1 Partitioning of Metals between Fractions in Urban Runoff.

In the case of Cd almost all the metal is contained in bioavailable forms (i.e. Electrochemically Available or Chelex Removeable and Exchangeable) with an average of 86.0% in these forms at Oxhey, 68% at Bergsjön and 73.3% for snowmelt at Bergsjön. The average percentages of the Electrochemically Available (35.9%) and Chelex Removeable (52.4%) Cd fractions for stormwater are increased significantly in snowmelt to 63.4% and 70.4% respectively, which is due to the Cd solubilising action of the high chloride levels. The average Strongly Bound fraction is higher at Bergsjön, in stormwater (22.7%) and snowmelt (23.8%), than at Oxhey (12.7%). However, as for Zn the Strongly Bound Cd fraction is quite variable, with the most significant percentages occurring in storms 7A and 7E, although for this metal storms 7H and 7I also contain a significant percentage of Strongly Bound Cd. As suggested in Section 6.3.3 the gullypot liquor and interstitial sediment water may influence the Strongly Bound Cd variations. For suspended solid Cd the Carbonate and Hydrous Metal Oxide and Organic fractions are relatively unimportant, but the Exchangeable fraction represents on average 24.6% of the total Cd in stormwater, but only 2.9% in snowmelt (due to the high loadings in the dissolved phase). This effect seems to be fairly consistent throughout the storm events studied. The pH/surface area dependent mechanism, described in Section 6.2.4, may provide a consistent influence on the partitioning of the Exchangeable Cd fraction.

Examination of Figure 7.1 shows that Pb is predominantly suspended solid associated. Only 9.6% of Pb is found in the dissolved phase of stormwater, although this increases to an average of 28.4% in snowmelt runoff. It should be noted that the snowmelt result is elevated by a high dissolved Pb flush (346.4 µg/l) during snowmelt 7I and that snowmelt 7J does not show elevated dissolved Pb proportions. Of the stormwater dissolved fractions, the Strongly Bound fraction is most important with a 5.4% contribution for Oxhey and 4.3% for Bergsjön. As with Zn and Cd the Strongly Bound fraction indicates gullypot liquor and interstitial sediment water mobilisation. The most significant proportions of Strongly Bound Pb are found in storms 7C, 7E and 7I.

The suspended solid phase is largely dominated by the Exchangeable fraction with 58.5% of Pb found in this phase at Oxhey and 64.6% at Bergsjön. Exchangeable Pb may be released into the water column when suitable conditions for solubilisation occur, such as heavy discharges of chloride in snowmelt or under reducing conditions in sediments. The Carbonate and Hydrrous Metal Oxide fraction indicates the mobilisation of reduced gullypot liquor and interstitial sediment water (see Section 6.3.3) and is significant for Pb in all the storms studied with an average contribution of 20.5%. The Organic Pb fraction is significant at Oxhey (14.1%) and in snowmelt at Bergsjön (9.4%), but is insignificant in stormwater at Bergsjön (2.8%).

Copper is fairly evenly distributed between both the dissolved and suspended solid phases. The Electrochemically Available fraction is more important at Bergsjön (13.2%) than at Oxhey (5.8%). The presence of free and weakly complexed metals may be modified by the pH range, which is generally higher at Oxhey. For storms 7A and 7B the pH range was between 7.1 and 7.6 which did not allow the presence of the Electrochemically Available fraction. There is a trend for a shift to more strongly complexed and adsorbed dissolved and suspended solid fractions. The same trend is seen at Bergsjön where the Electrochemically Available Cu fraction is significant in storms 7E, 7G and 7H (pH range 6.1 - 6.8), but less significant in storm 7F (pH range 6.9 - 7.2). These findings agree with experiments on Cu adsorption to solids which show that dissolved Cu is adsorbed at pH values greater than 5.5, with 100% adsorption at approximately pH 7.0 (see Section 2.7.2.1). Electrochemically Available Cu is less dependent on pH in snowmelt where the high dissolved chloride concentrations compete successfully with solid adsorbed Cu to give an average of 23.3% in this fraction. However, a heavy flush of suspended solids in snowmelt 7I (up to 1624.1 mg/l) caused a reduction of Electrochemically Available Cu in this event.

Chelex Removeable Cu is significant in both stormwater and snowmelt with, on average, a contribution of 31.9%. However the Strongly Bound fraction is more variable and, as with the other metals, is an

important indication of gullypot liquor and interstitial sediment water mobilisation (see Section 6.3.3). The most significant proportions of Strongly Bound Cu are found in storms 7A and 7E.

In the Swedish catchment the suspended solid Cu concentration is higher and in stormwater this is reflected in the Exchangeable fraction which comprises 35.2%, as compared to 15.8% at Oxhey. The Carbonate and Hydrous Metal Oxide fraction may originate from any part of the stormwater system although, as with Pb, the amounts may be dependent on hydrous Fe and Mn oxide formation in the gullypot. The 16.5% average value for Cu is exceeded in storms 7A, 7F, 7G and 7H and the trend closely follows that for Pb in the same fraction. The Organic fraction is more important in stormwater at Oxhey (17.5%) than at Bergsjön (6.0%) although snowmelt at Bergsjön (25.4%) is also important. For snowmelt 7I the Organic fraction is considerably more important than snowmelt 7J and this may be due to the high particulate organic carbon in the former (22.4 - 33.5%) compared to 7J (5.9 - 12.9%).

## 7.2 Loading Variations of Heavy Metal Species through Urban Hydrographs.

The storm events studied show distinct trends for heavy metal loadings, especially when considered in terms of the loading of metal fractions onto the hydrograph. Six of the storm events, each containing at least nine samples, have been selected for further analysis.

### 7.2.1 Hydrographic and Controlling Parameter Variations through the Selected Storm Events.

In order to understand metal variations through the storm events it is first necessary to describe the flow and controlling parameter changes through each event. Of the six storm events discussed in this section, two represent stormwater at Oxhey, two are stormwater at Bergsjön and two are snowmelt at Bergsjön.

7.2.1.1 Storm 7A.

This Oxhey storm of just over two hours duration exhibits three flow peaks with a maximum flow in the second peak of 231 l/s (Figure 7.2). Suspended solid loadings clearly follow the flow peaks, but with noticeable exhaustion for the final hydrograph rise.

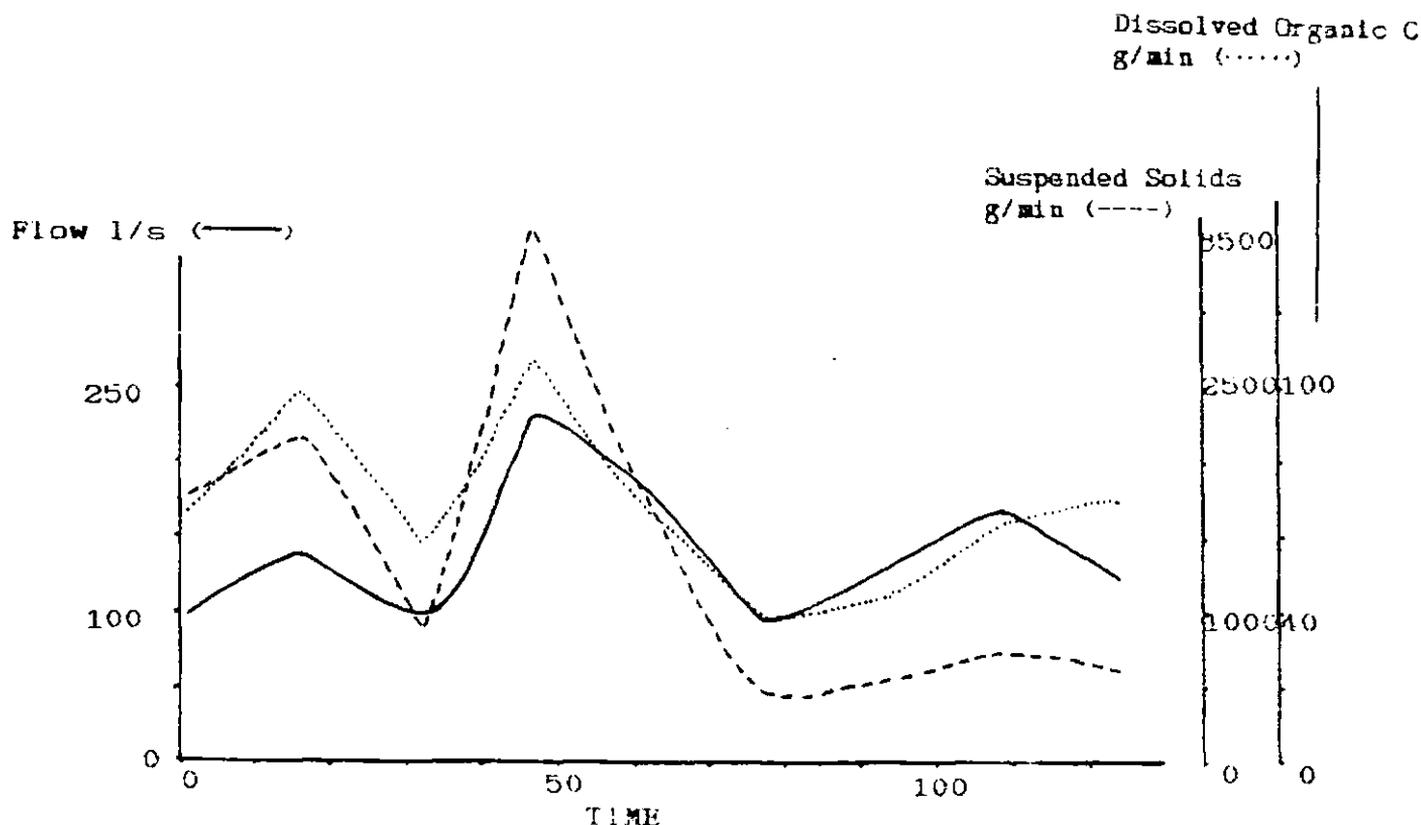


Figure 7.2 Hydrograph and Parameter Loadings, Storm 7A.  
Time in Minutes Commencing 02.58

Dissolved chloride (not shown) is washed out with the first flow peak and consequently dilution-exhaustion results after 30 minutes. This washoff profile is not observed for dissolved organic carbon. As discussed for gullypot outflow in Sections 6.3.1.1 and 6.3.1.3, the first dissolved organic carbon peak may be related to the mobilisation of in-pipe solids washoff, road runoff, gullypot liquor and interstitial sediment water. The second and third organic carbon peaks can arguably be related to the mobilisation of gullypot sediment maturation products and organics from the road surface. Physical

mobilisation of sediments is therefore important for the liberation of matured organic compounds, particularly in decomposing gullypot and in-pipe sediments. Dissolved organic carbon released by physical mobilisation may be termed residual matured organics, while dissolved organic carbon quickly washed through the system may be termed readily washed organics.

7.2.1.2 Storm 7B.

This storm, of nearly three hours duration and coming only two days after 7A, is characterised by an early flow peak giving a characteristic "first flush" of pollutants (Figure 7.3).

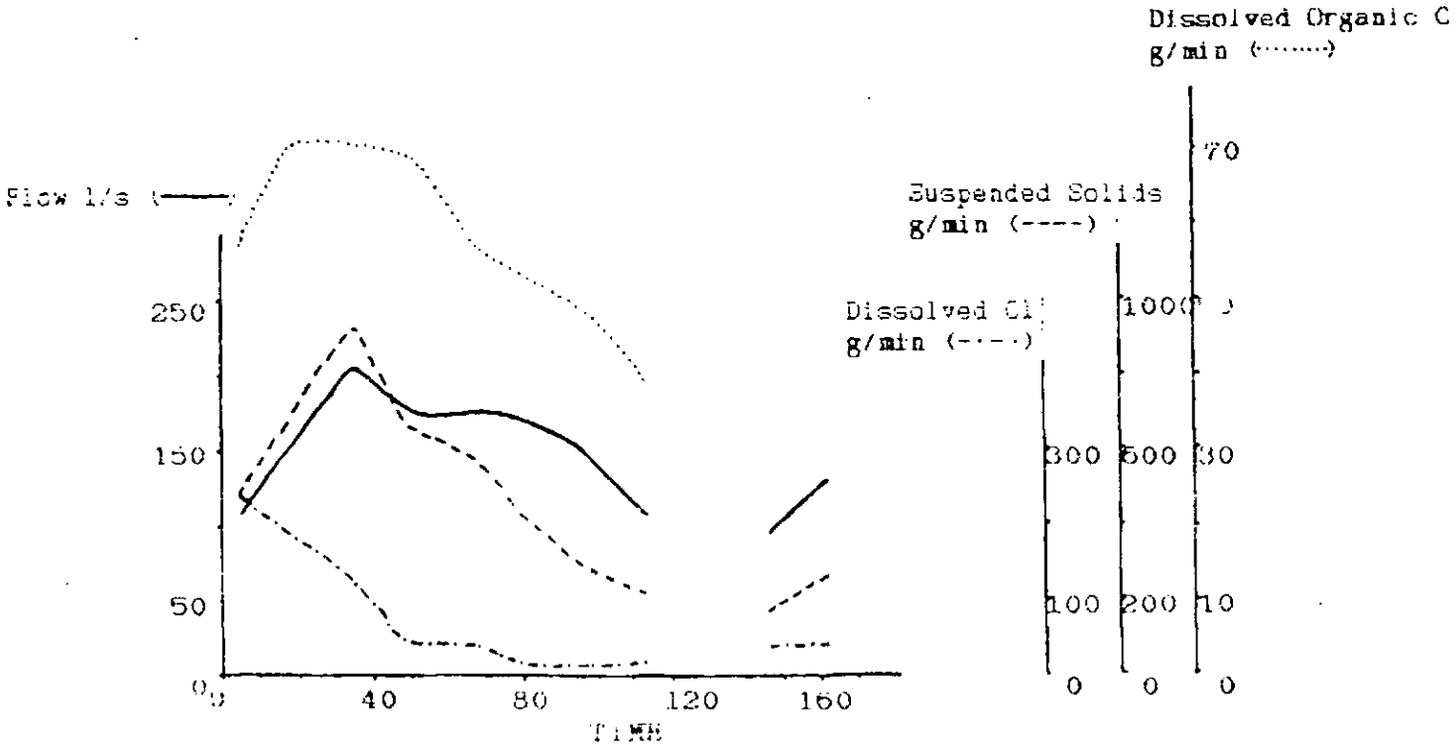


Figure 7.3 Hydrographic and Parameter Loadings, Storm 7B.  
Time in Minutes Commencing 23.48

Dissolved chloride is clearly rapidly washed out, while the dissolved organic carbon peak is prolonged due to contributions from residual matured organics. Suspended solids follow the flow profile although, from the gullypot study (see Section 6.3.1), a more pronounced "first

flush" of solids on the rising limb of the hydrograph might be expected. It can be deduced that, on such a large catchment as Oxhey, different contributing areas make up the storm profile and therefore the suspended solids peak may represent the first contribution from certain catchment sub-areas.

### 7.2.1.3 Storm 7F.

This Bergsjön storm of nearly 1½ hours duration is characterised by a low flow rate period before the main storm event (Figure 7.4). During this period readily washed organics provide an important flush of dissolved organic carbon and probably also produce the organic peak on the rising limb of the hydrograph. The secondary organic peak, just after peak flow, may provide evidence of residual matured organics mobilisation.

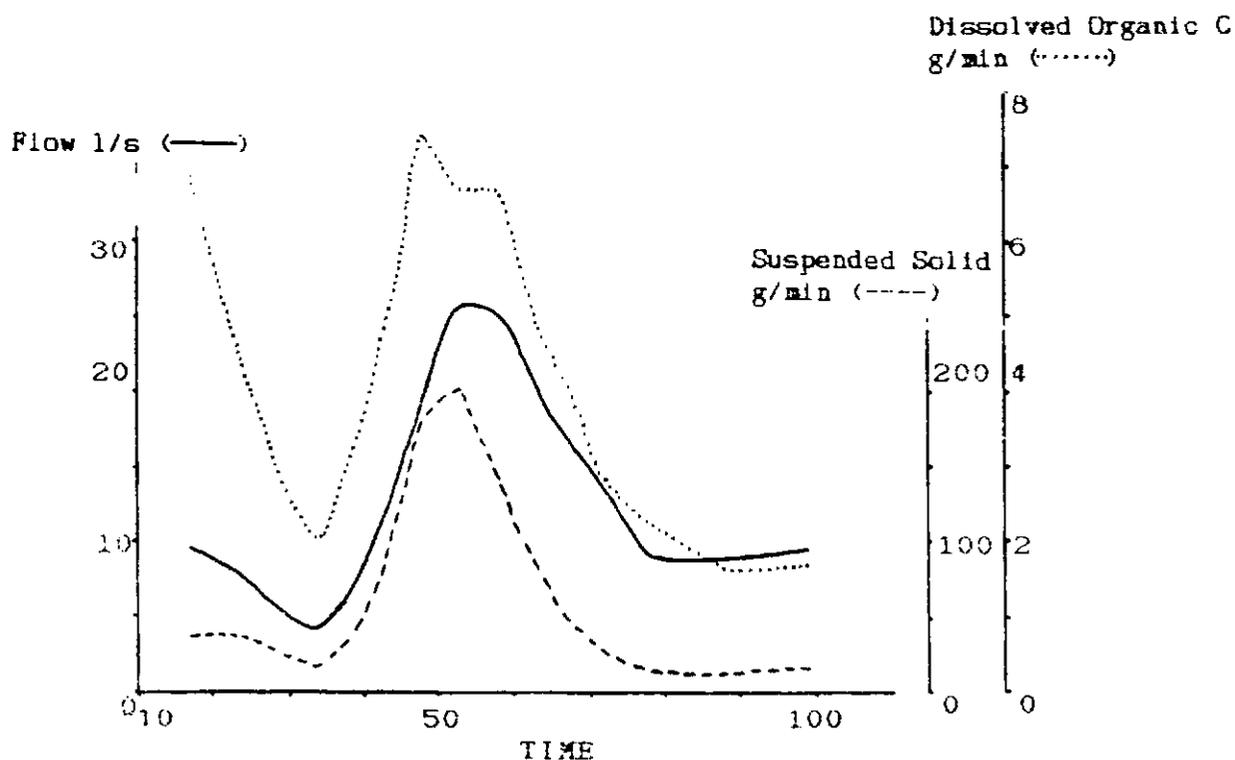


Figure 7.4 Hydrograph and Parameter Loadings, Storm 7F.  
Time in minutes Commencing 15.30

The first suspended solids peak may represent the early mobilisation of gullypot solids, as well as relatively easily mobilised solids from

road runoff and particularly in-pipe washout. The main solids peak shows evidence of peaking with, or even slightly before, peak flow, which agrees with findings from the gullypot study (see Section 6.3.1) i.e. the "first flush" of solids from road runoff is delayed by gullypot settling, but is re-mobilised by increasing flow on the rising limb of the hydrograph. In addition in-pipe sediments may also be a significant, if not the most important, feature of early sediment washout.

7.2.1.4 Storm 7H.

This second Bergsjön storm event of nearly five hours duration contains two major peaks of flow (Figure 7.5). Suspended solids loadings tend to follow the hydrograph closely, apart from an early flush of suspended solids which slightly precedes the second flow peak.

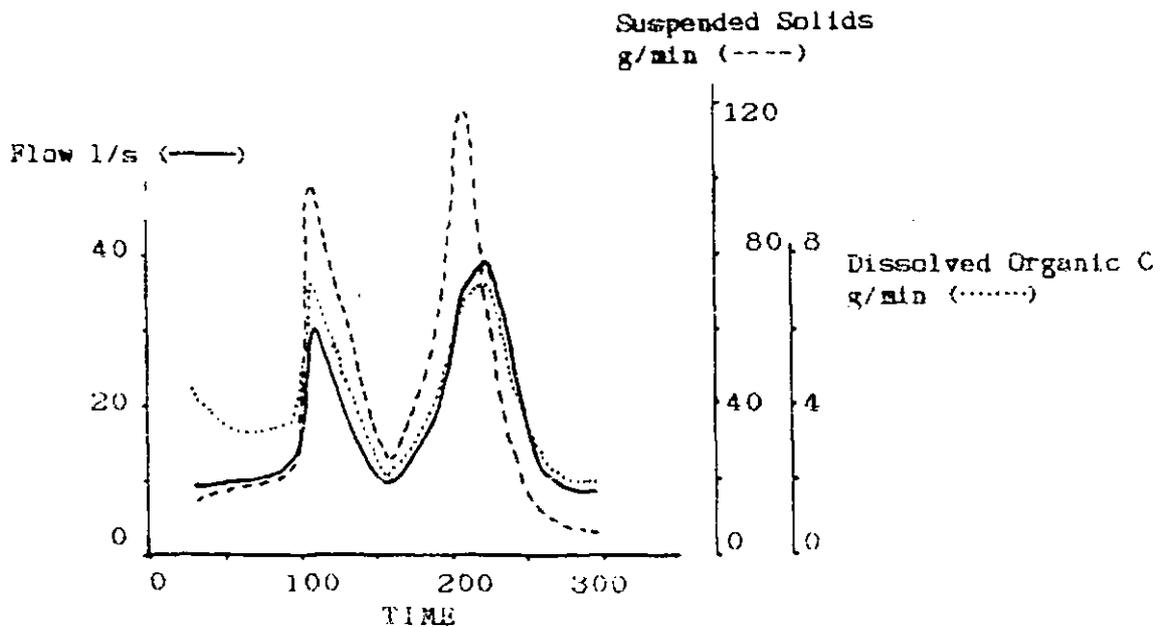


Figure 7.5 Hydrograph and Parameter Loadings, Storm 7H.  
Time in Minutes Commencing 13.00

Dissolved organic carbon follows flow throughout the storm. At the beginning of the storm event a flush of readily washed organics can be seen and these compounds may contribute significantly to the two main peaks. However the broadening of the second peak, which follows flow, may be related to residual matured organics mobilisation.

7.2.1.5 Storm 71.

Storm 71 was a snowmelt of nearly seven hours duration (Figure 7.6). The early low flow snowmelt period of nearly six hours was followed by a light rainfall event of 0.2 mm/hour intensity which greatly increased the flow. Snowmelt continued during the recession limb of the hydrograph.

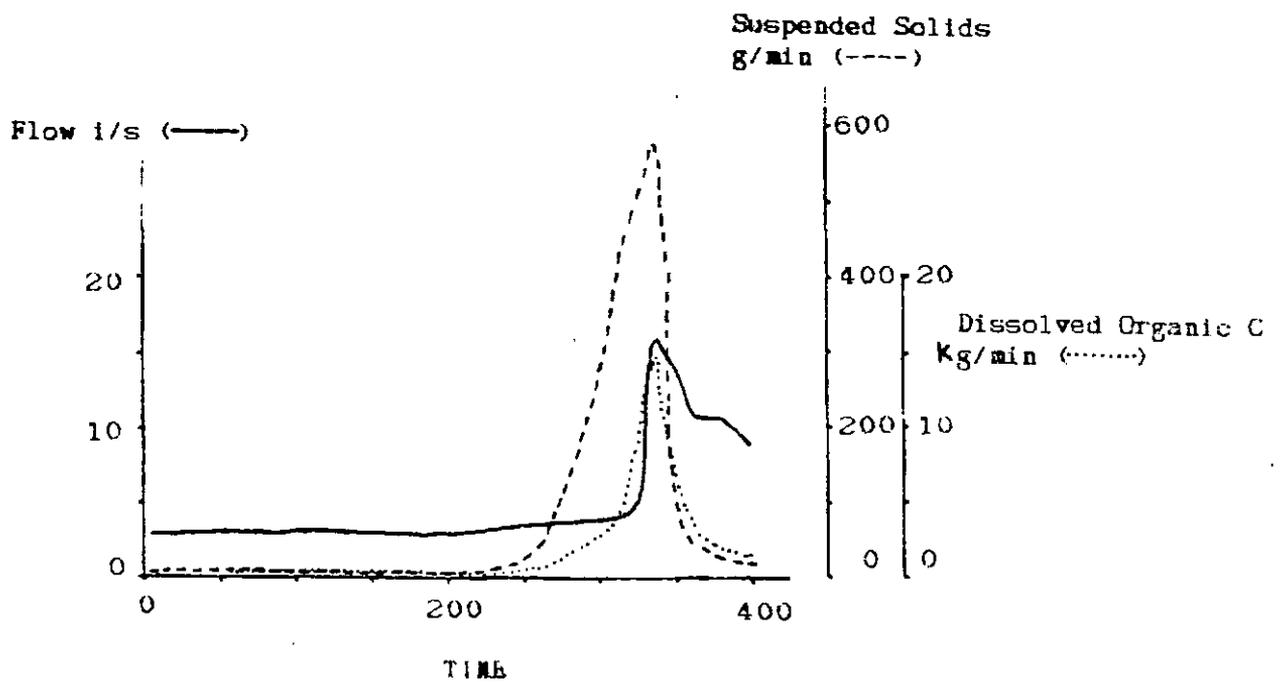


Figure 7.6 Hydrograph and Parameter Loadings, Storm 71.  
Time in minutes Commencing 13.50

Suspended solid loadings start to increase before flow, demonstrating the rapid washoff of snow bound particulates. Dissolved chloride concentrations were high throughout the snowmelt event (3.4-17 g/l),

with a peak loading of 14.5 Kg/min corresponding to peak flow (total storm dissolved chloride loading was 687 Kg).

7.2.1.6 Storm 7J.

Storm 7J represents a small ten hour section of a long continuous snowfall/snowmelt period which lasted during the greater part of January-April 1985. High dissolved chloride levels (1.0-1.3 g/l) throughout the snowmelt suggest that de-icing salts are responsible for the snowmelt (Figure 7.7).

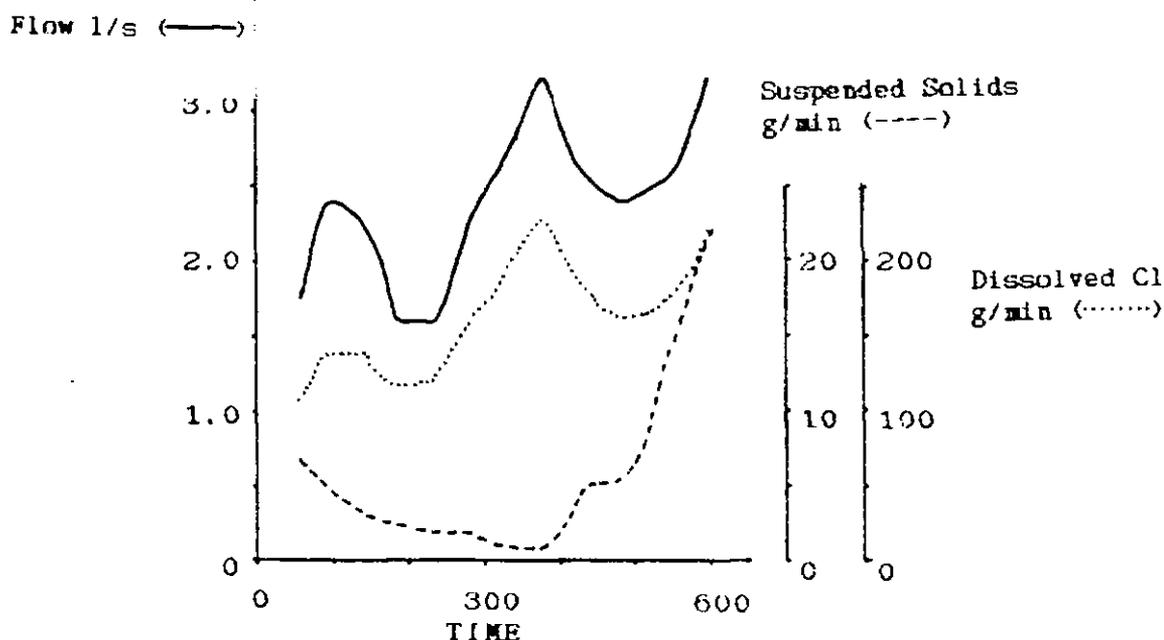


Figure 7.7 Hydrographic and Parameter Loadings, Storm 7J.  
Time in Minutes Commencing 20.00

The increase of flow after 500 minutes is due to the commencement of warmer daytime temperatures and, possibly, emulsification of the snow and salt lying on the road by early morning traffic. Suspended solids loadings increase sharply after 500 minutes which suggests that much of the suspended solids are derived from snow bound particulates.

### 7.2.2 Loading Variations for Individual Metal Fractions.

Individual metal species often load onto the storm hydrograph at different rates, which can be explained in terms of the controlling parameters (discussed in Section 7.2.1) and also the influence of mobilisation and transport processes. In order to interpret the loading of individual metal fractions onto the chemographs the predominant metal fraction is identified on the chemograph as outlined in Section 6.3.2 (Figure 6.24). In addition Table 6.14 was frequently consulted to identify the possible sources, prior to release from the gullypot, of metal fractions. Despite the limitations of comparing results between urban catchments with different characteristics, this proves to be a useful approach. One explanation for this apparent contradiction is that the physical and chemical processes outlined in Section 6.2 do not change between urban catchments, it is the degree to which they occur which changes.

#### 7.2.2.1 Dissolved Zinc Fractions.

The variations in loadings of dissolved Zn during three storm events are shown in Figure 7.8. Generally the Chelex Removeable fraction dominates due to the dissolution and acid rain mobilisation of Zn from road surface dusts. However, the Strongly Bound fraction often shows unexpected contributions. It should be noted that the Electrochemically Available and Chelex Removeable fractions usually peak together and cannot be separated in terms of different origins and processes.

For storm 7A (Figure 7.2 and Figure 7.8(a)) the first Chelex Removeable Zn peak at the commencement of the storm is typical of the rapid "first flush" due to the solubilisation of Zn from road surface and in-pipe sediments as well as gullypot liquor mobilisation. Further Chelex Removeable peaks can also be related to the acid rain mobilisation of road, gullypot and in-pipe sediments. Strongly Bound Zn is significant when the heaviest flow occurs and can be accounted for by the physical mobilisation of gullypot interstitial sediment

water, which agrees with the interpretation of dissolved organic carbon loadings. The second Strongly Bound Zn peak arrives late in the storm and can be accounted for by a variable contributing area concept. This fraction has taken longer to arrive from gullypots on the edges of the catchment.

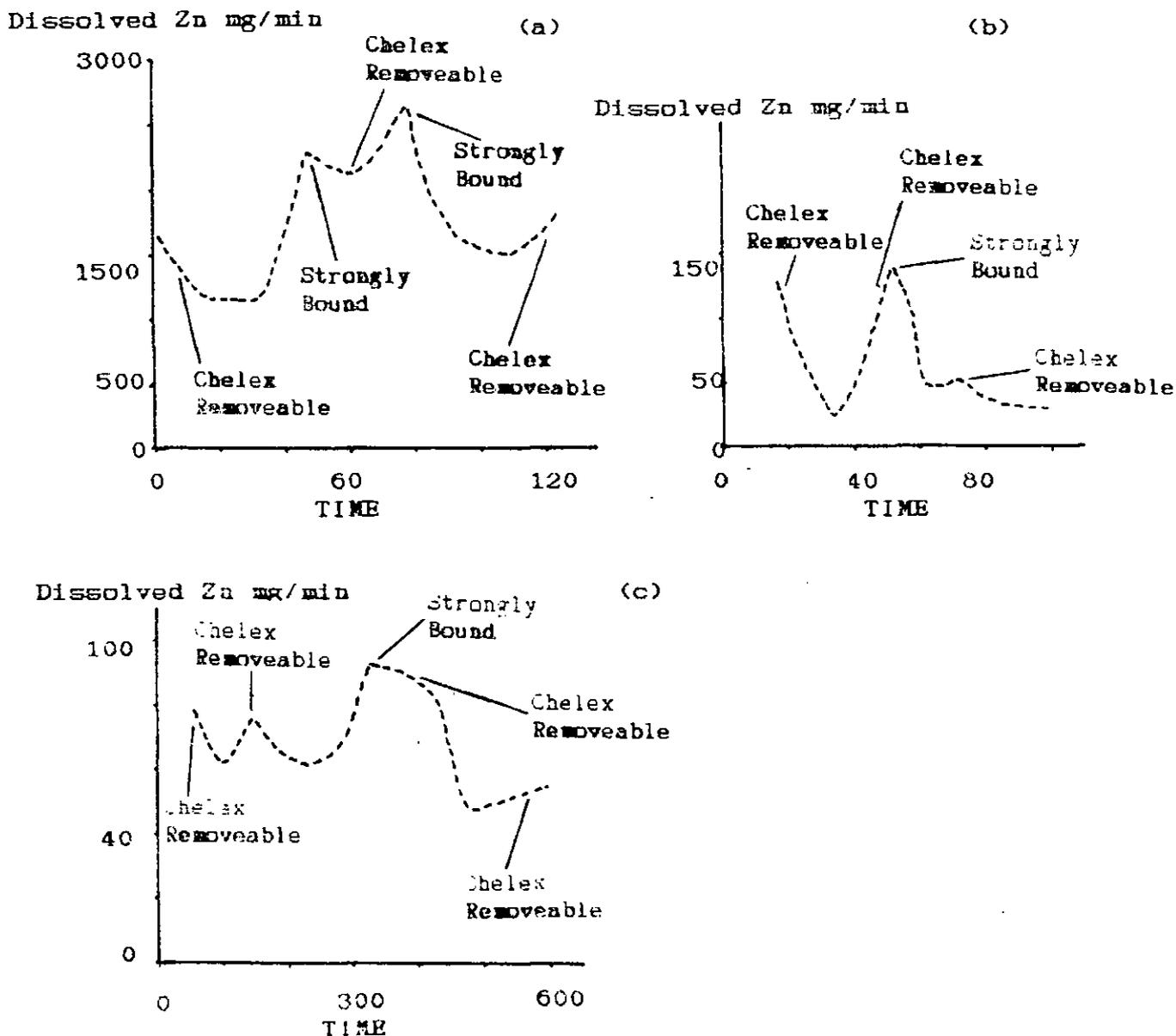


Figure 7.8 Dissolved Zinc Loadings for Selected Events.  
Time in Minutes

Storm 7F (Figure 7.4 and Figure 7.8(b)) is on a different catchment but the Zn fractions behave in a similar way. Both dissolved organic carbon and Chelex Removeable Zn exhibit a "first flush" at the beginning of the storm and on the rising limb of the hydrograph, due to sedimentary Zn solubilisation and gullypot liquor mobilisation

processes. The late Chelex Removeable peak is almost certainly due to the acid rain washing of road, gullypot and in-pipe sediments, as it lacks an interpretation from the hydrograph or controlling parameters. The Strongly Bound Zn occurs just at and after peak flow, together with the suspected residual matured organics peak, and may therefore be a result of gullypot interstitial sediment water mobilisation.

High dissolved chloride levels may also release Zn from solids into the Chelex Removeable fraction. During snowmelt 7J (Figure 7.7 and Figure 7.8(c)) oscillating loading curves of Chelex Removeable Zn represent the chemical mobilisation of road surface snow bound solid Zn by dissolved chloride in snowmelt runoff. A peak of Strongly Bound Zn is found which may be a gullypot product.

During snowmelt event 7I, which is characterised by a small rainfall (Figure 7.6 and Figure 7.9), Electrochemically Available Zn exhibits early small peaks and a delayed response for the main peak compared to the other parameters. Thus Zn is present in its lowest Electrochemically Available loading at the onset of the rainfall event, after  $\approx$  300 minutes. High suspended solid and particulate organic carbon concentrations probably control the partitioning of Zn at this stage and hence limit Electrochemically Available Zn levels.

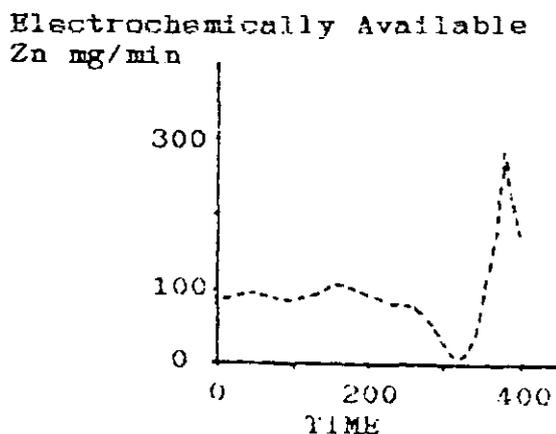


Figure 7.9 Dissolved Zinc Loadings in Snowmelt 7I.  
Time in Minutes

7.2.2.2 Dissolved Cadmium Fractions.

Dissolved Cd was reported in Chapter 6 to have a significant contribution from Strongly Bound species originating from the gullypot liquor and interstitial sediment water.

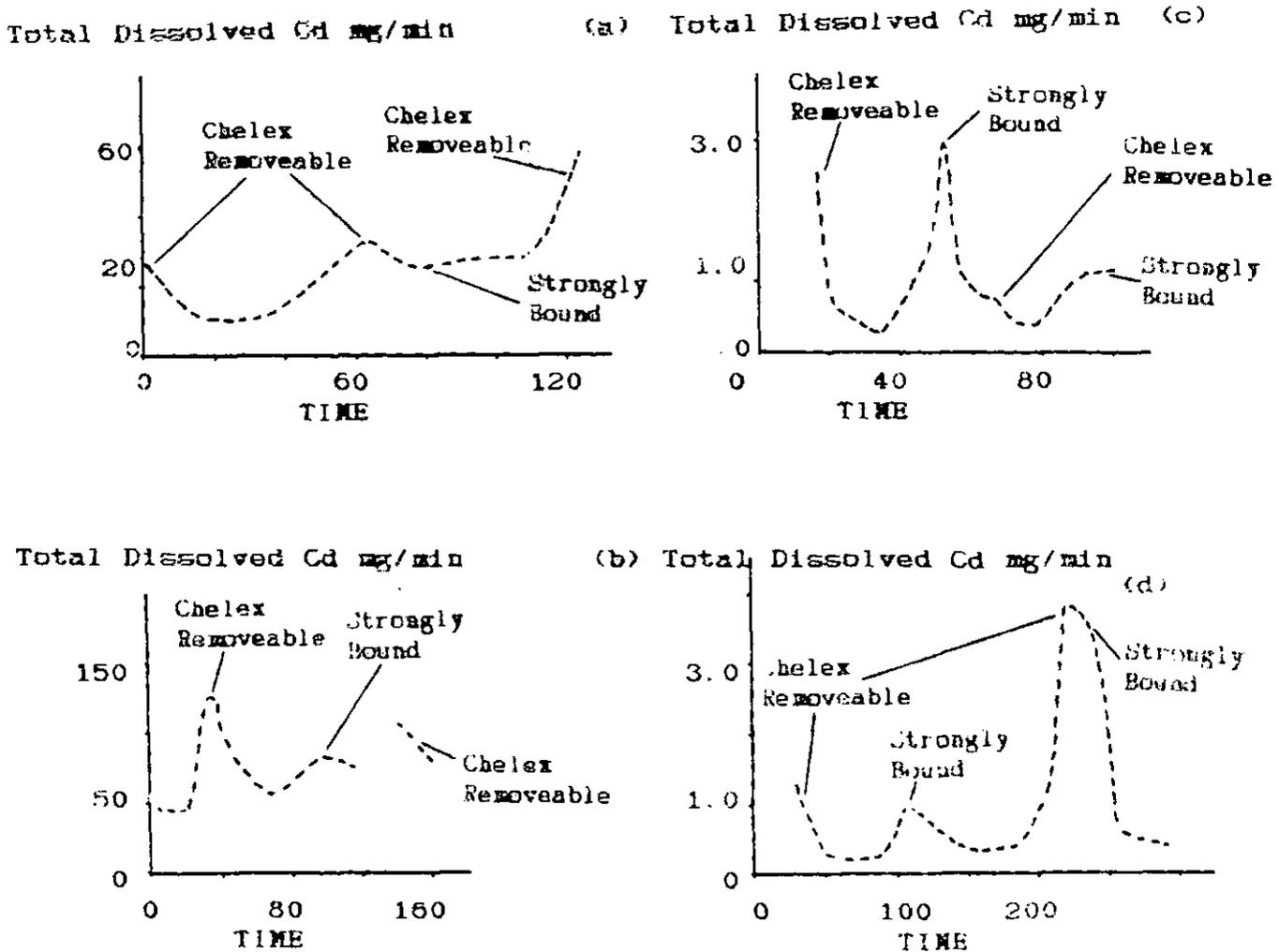


Figure 7.10 Dissolved Cadmium Loadings for Selected Storm Events.  
Time in Minutes

In storm 7A (Figure 7.2 and Figure 7.10(a)) a "first flush" of Chelex Removeable Cd is seen which may originate from the solubilisation of road and in-pipe sedimentary Cd, as well as gullypot products. Acid rain Cd mobilisation may account for the later peaks. The Strongly

Bound fraction occurs as a late peak in the storm profile representing gullypot interstitial sediment water mobilisation.

For storm 7B (Figure 7.3 and Figure 7.10(b)) rapidly washed off Chelex Removeable Cd is not significant at the very beginning of the storm. As only two days had elapsed since storm 7A some dilution-exhaustion of readily solubilised Cd may have occurred. The lower suspended solids loadings in storm 7B, compared to storm 7A, tend to suggest that in-pipe sediments may have been thoroughly washed out of the system. Therefore the Chelex Removeable Cd is dominated by the acid rain mobilisation of road dusts and appears as a peak coincident with flow and in a late section of the storm. Strongly Bound Cd is found nearly one hour after peak flow which means that this is due to a late mobilisation process rather than a longer distance source contribution (the time of concentration for Oxhey being 19.2 minutes).

In storm 7F (Figure 7.4 and Figure 7.10(c)) the readily washed off Chelex Removeable Cd species are observed first in the storm profile, with another contribution at 67 minutes after peak flow due to the acid washing of urban sediments. An important Strongly Bound Cd peak is found at peak flow corresponding to gullypot interstitial sediment water mobilisation. The late Strongly Bound Cd peak may suggest that the interstitial sediment water was not completely washed out by the first flow peak and was further mobilised late in the storm event.

In storm 7H (Figure 7.5 and Figure 7.10(d)) the Chelex Removeable Cd fraction shows a small "first flush" for sediment solubilisation and gullypot liquor, but is more significant on the rising limb of the second flow peak. This can be related to the acid washing of gullypot and road sediments. Strongly Bound Cd dominates the first flow peak and is also important in the second flow peak. This suggests that the mobilisation of gullypot interstitial sediment water can contribute significant loadings of Strongly Bound Cd to stormwater.

Two snowmelt events are presented in Figure 7.11, showing Electrochemically Available Cd loading variations.

Electrochemically Available  
Cd mg/min (b)

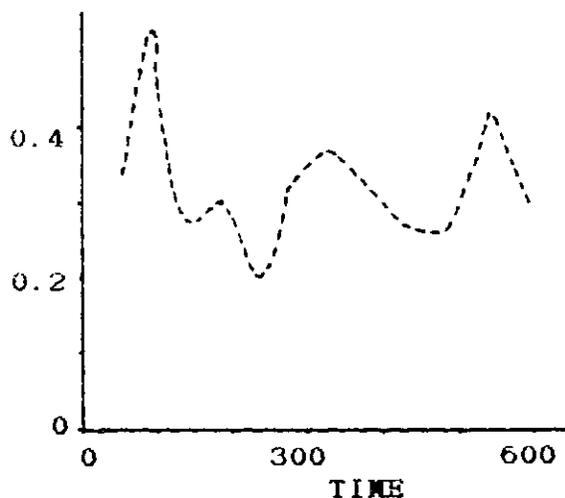
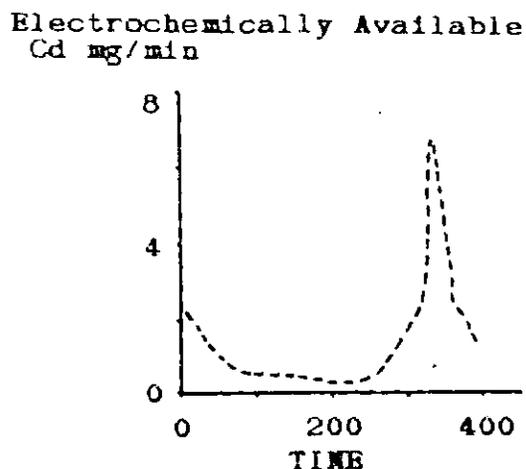


Figure 7.11 Electrochemically Available Cadmium Loadings through two Snowmelt Events.  
Time in Minutes

Bioavailable Cd in snowmelt 7I (Figure 7.6 and Figure 7.11(a)) has similar loading variations to dissolved chloride, although with a flush at the beginning of the snowmelt (concentrations up to 12.5  $\mu\text{g/l}$ ). At the onset of rainfall a high suspended solids concentration occurred, but these solids were stripped of Cd by the associated high chloride levels. The result was a rapid rise in the loading of bioavailable dissolved Cd which attained a peak concentration of 8.0  $\mu\text{g/l}$ .

The ease of Cd washoff is also seen for the second prolonged snowmelt 7J (Figure 7.7 and Figure 7.11(b)). The loading variations do not follow flow or the controlling parameters but oscillate between 0.2 and 0.55 mg/min.

#### 7.2.2.3 Dissolved Lead Fractions.

Dissolved Pb fractions show similar incoming distributions to those of Zn and Cd.

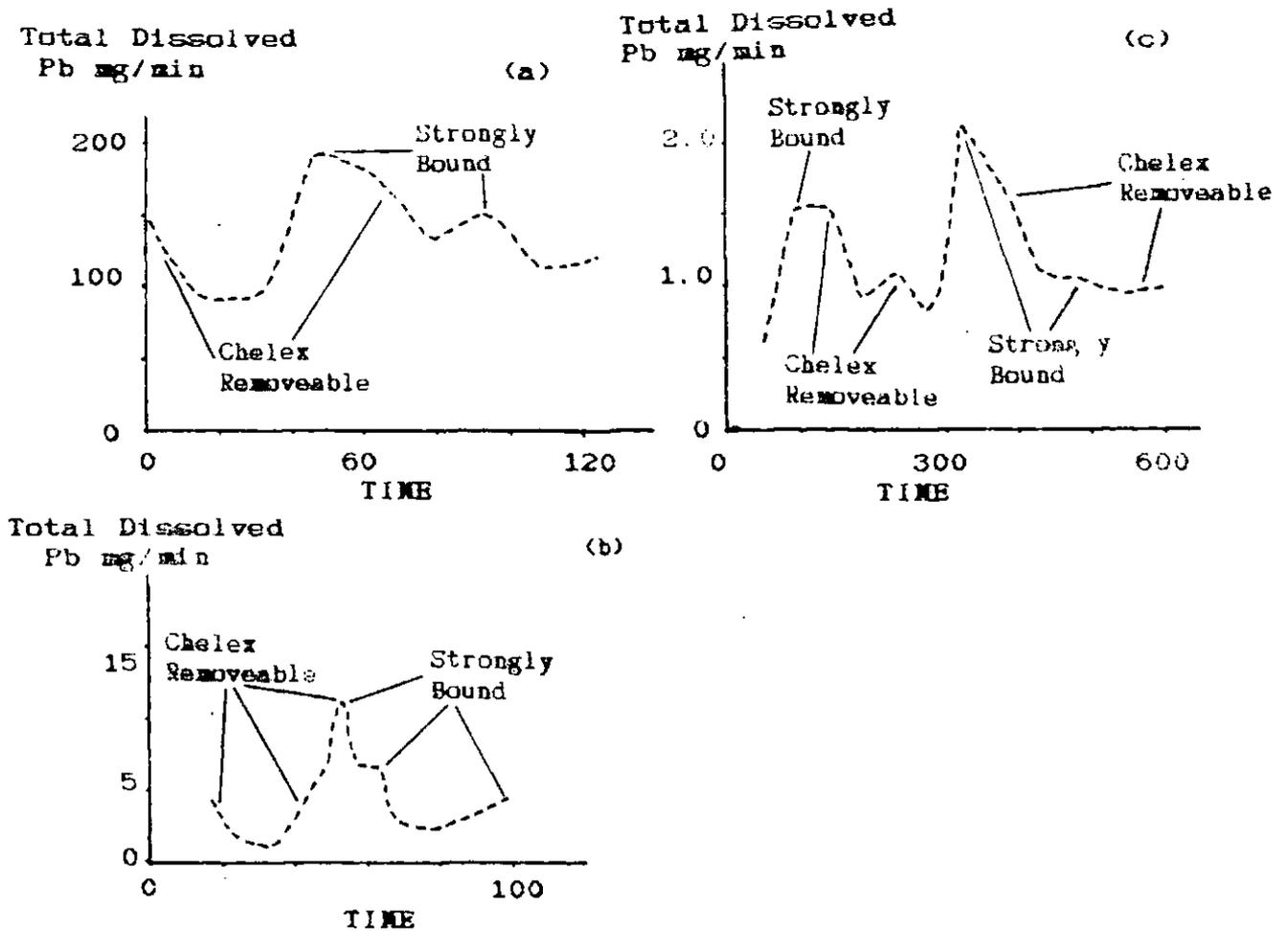


Figure 7.12 Dissolved Lead Loadings for Selected Events.  
Time in Minutes

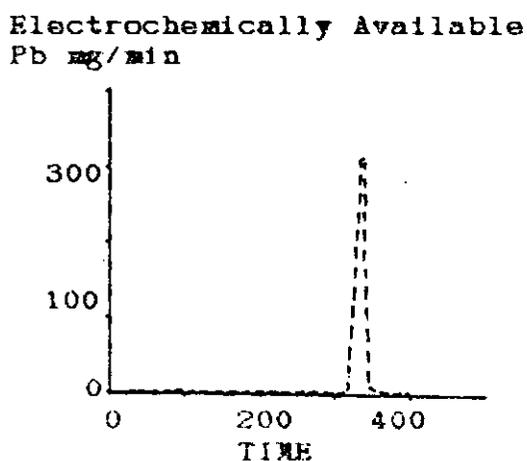
In storm 7A (Figure 7.2 and Figure 7.12(a)) Chelex Removeable Pb shows the typical first washoff from sediment solubilisation and gullypot liquor, with a second peak after the second flow maximum related to acid rain mobilisation. The first Strongly Bound peak (corresponding to peak flow), which was not very prominent for either Zn or Cd, was the most significant Pb peak. In this case, therefore, Strongly Bound Pb may be acting as a tracer for the mobilisation of the interstitial sediment water of gullypots which have service roads with regular traffic. The second Strongly Bound Pb peak appears at a later stage on

the chemograph than for either Zn or Cd, and may represent an input corresponding to the third flow peak.

Storm 7F (Figure 7.4 and Figure 7.12(b)) shows similar dissolved Pb fraction distributions to those found for Zn and Cd. Chelex Removeable Pb dominates the early storm profile giving a similar distribution to the removal of readily washed organics. Strongly Bound Pb dominates the second half of the storm profile representing the washing out of gullypot interstitial sediment water.

For snowmelt 7J (Figure 7.7 and Figure 7.12(c)) oscillating Chelex Removeable Pb and Strongly Bound Pb peaks are observed. The Chelex Removeable peaks may be most indicative of the release of road surface snow bound metal, while the Strongly Bound fraction may be physically mobilised sporadically from the gullypots. The oscillation pattern may be related to the intermittent nature of snow melting.

Figure 7.13 Electrochemically Available Lead Loadings during Snowmelt 7I.  
Time in Minutes



During snowmelt event 7I (Figure 7.13) Electrochemically Available Pb loadings reach a peak of 315 mg/min, as compared to the 0.42 mg/min in

snowmelt 7J. The peak corresponds to the heavy flush of dissolved chloride in this storm (Figure 7.6) and may be due to the chloride controlled release of Pb from road, gullypot and suspended stormwater solids.

#### 7.2.2.4 Dissolved Copper Fractions.

The Chelex Removeable fraction usually dominates the loading profile of dissolved Cu during storm events. However, late Strongly Bound flushes can change the profile significantly in some cases.

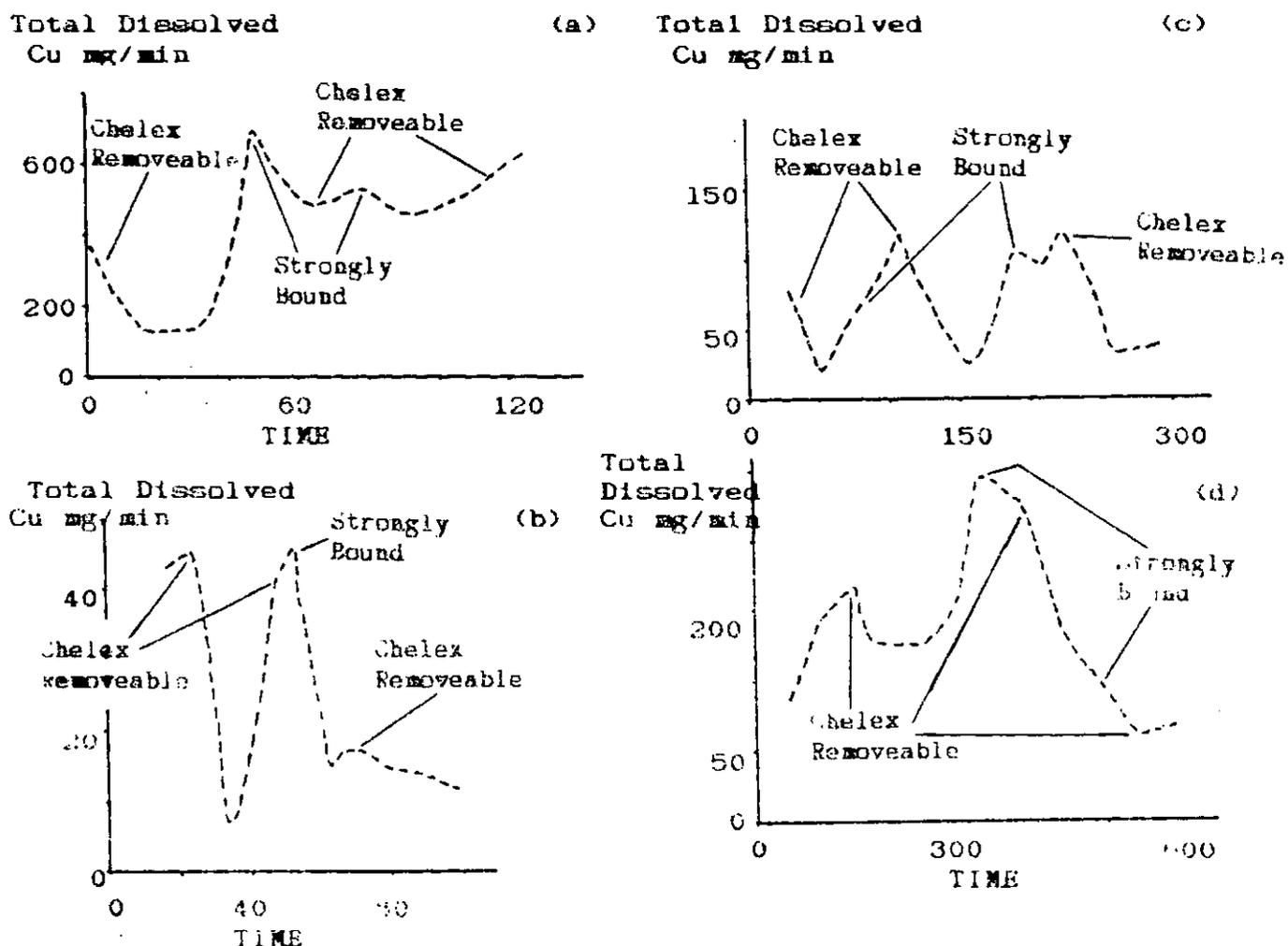


Figure 7.14 Dissolved Copper Loadings for Selected Events.  
Time in Minutes

In storm 7A (Figure 7.2 and Figure 7.14(a)) Chelex Removeable Cu exhibit a "first flush", due to sedimentary Cu solubilisation and gullypot liquor contributions, and secondary peaks from acid rain mobilisation, as was found for the other three dissolved metals. The first Strongly Bound Cu peak, from gullypot interstitial sediment water mobilisation, arrives with the second major flow peak. The second Strongly Bound Cu peak arrives at the same time as the Strongly Bound Zn and Cd peaks and can be accounted for by a variable contributing area concept.

Storm 7F (Figure 7.4 and Figure 7.14(b)) requires a different interpretation as much of the dissolved Cu comes from the abundant Cu guttering within the Bergsjön catchment. At the start of the storm a significant early peak, corresponding to low flow, is observed. This may be attributed to the acid washing of roof guttering and contaminated in-pipe sediments, yielding Chelex Removeable Cu species. Subsequent Chelex Removeable Cu peaks can be related to this source. Road dust contributions are not so important on this catchment as 80% of Cu comes from the corrosion of Cu guttering (Malmqvist 1983). The Strongly Bound Cu fraction arrives with the peak of residual matured organics and therefore suggests an origin of gullypot interstitial sediment water. Many of the gullypots on the catchment are entered below ground by a roof runoff pipe. Therefore the Strongly Bound Cu fraction may originate from gullypot interstitial sediment water which is contaminated with roof runoff Cu.

In storm 7H (Figure 7.5 and Figure 7.14(c)) a primary Chelex Removeable Cu peak represents the early acid washing of roof surfaces and in-pipe sediments. During the two major flow peaks of the storm Strongly Bound Cu loads onto the chemograph on the rising limb of the hydrograph, while Chelex Removeable species appear in more significant loadings at peak flow. The Strongly Bound Cu peaks may represent the washing out of the roof runoff contaminated interstitial sediment water which has been stirred up into the gullypot liquor between storm events. The Chelex Removeable peaks do not show any exhaustion between

storm peaks which is due to the continual acid rain mobilisation of dissolved Cu from guttering.

Snowmelt 7J (Figure 7.7 and Figure 7.14(d)) has similar dissolved Cu variations to dissolved chloride and flow and thus differs from the other dissolved metals. It is probable in this case that the high dissolved chloride concentrations continually desorb Cu from below ground sediments and depend on a relatively long contact time between melted snow and the sediment. However, when snowmelt increases a dilution effect occurs, as well as a reduction of contact time and therefore dissolved Cu loadings decrease towards the end of the storm. Chelex Removeable Cu usually dominates the profile, probably as chloride species of Cu. Strongly Bound Cu may represent gullypot products entering the profile.

Chelex Removeable Cu (Figure 7.6 and Figure 7.15) follows a similar trend to bioavailable Zn in snowmelt 7I. The increase of bioavailable metal, observed for Cd and Pb, with rising chloride concentrations and loadings is offset by adsorption onto the high suspended solids loadings released during the rainfall event. Consequently the highest bioavailable Cu loadings occur during sustained low flow snowmelt.

Chelex Removeable  
Cu  $\mu\text{g}/\text{min}$

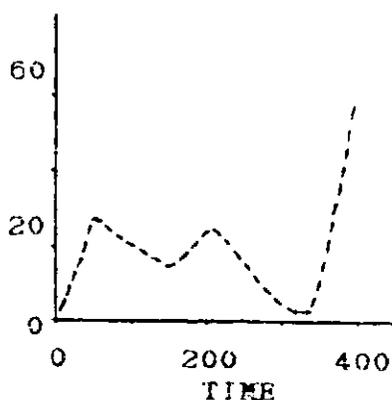


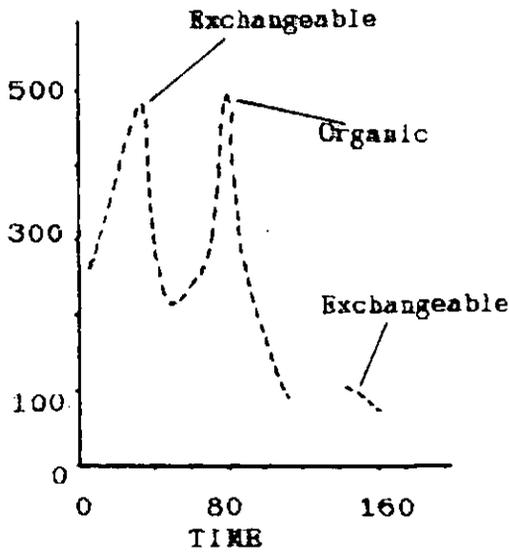
Figure 7.15 Snowmelt 7I Variations of Chelex Removeable Copper.  
Time in Minutes

7.2.2.5 Suspended Solid Zinc Fractions.

Suspended solid associated Zn tends to follow the suspended solids through the hydrograph. However, a broadening of the Zn loading peaks is often observed which can be attributed to the late entry of certain fractions. The Exchangeable fraction usually dominates the profile, although the Carbonate and Hydrous Metal Oxide and Organic fractions also show importance at certain points in the storm profiles.

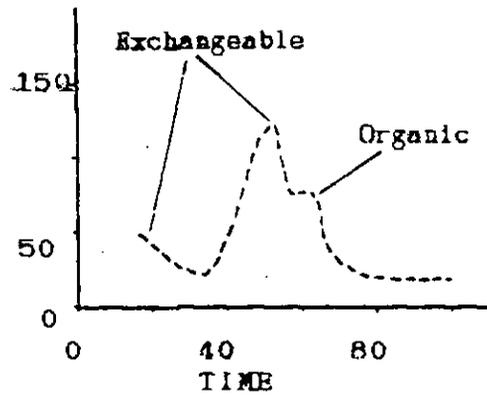
Total Solid  
Zn mg/min

(a)



Total Solid  
Zn mg/min

(b)



Total Solid  
Zn mg/min

(c)

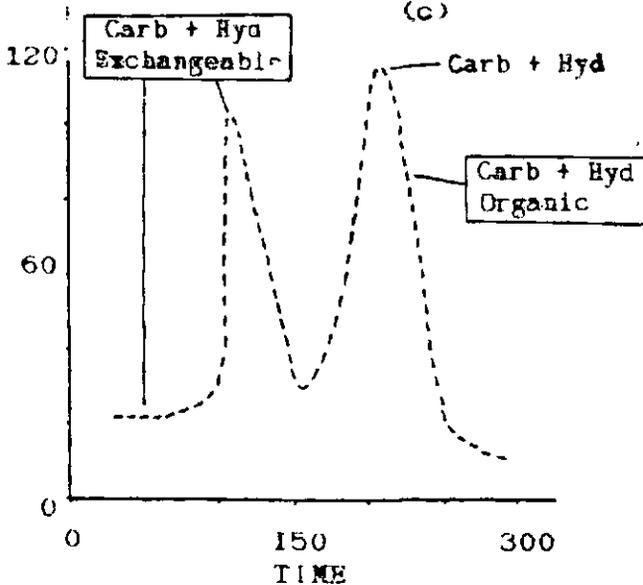


Figure 7.16 Total Solid Zinc Loadings for Selected Events.  
Time in Minutes

In storm 7B (Figure 7.3 and Figure 7.16(a)) a first peak relating to road and in-pipe sediment washoff is found which follows suspended solids loadings. Although not indicated in Figure 7.16(a), the Carbonate and Hydrous Metal Oxide Zn fraction also reaches maximum loadings at this point, with a value of 52.5 mg/min, which may be due to gullypot liquor solids and reduced interstitial sediment water mobilisation and oxidation. However, through the in-pipe system the Exchangeable fraction becomes much more significant, probably due to the action of the pH/surface area dependent solid Zn uptake (see Section 6.2.4), which tends to obscure the origin of the Zn fractions. The second Zn peak, largely containing the Organic fraction and probably derived from gullypot basal sediment, is as significant in magnitude as the first peak. However, this Organic peak is found late in the hydrograph when flow is starting to decrease and may be explained by a late entrainment of gullypot basal sediments.

In storm 7F (Figure 7.4 and Figure 7.16(b)) the Exchangeable fraction, from road runoff and other storm solids enriched with surface bound Zn, dominates the first half of the storm. An Organic peak again appears late in the storm profile, after peak flow, due to late contributions of gullypot solids.

All three solid fractions contribute significantly to storm 7H (Figure 7.5 and Figure 7.16(c)). At the beginning of the storm the Exchangeable and Carbonate and Hydrous Metal Oxide fractions dominate solid Zn washoff and represents inputs from road runoff, gullypot liquor and in-pipe solids. The second flow peak is more intense and may mobilise gullypot sediments which accounts for the domination of the Carbonate and Hydrous Metal Oxide and Organic fractions.

#### 7.2.2.6 Suspended Solid Cadmium Fractions.

The suspended solid associated Cd loadings usually show similar trends to suspended solids through the hydrographs. The Exchangeable fraction often completely dominates the chemograph for Cd showing inputs due to road surface runoff, gullypot liquor and basal sediments. The

Carbonate and Hydrated Metal Oxide fraction was rarely detectable, but the Organic fraction indicates the occurrence of gullypot interstitial sediment water mobilisation (and therefore the finer sediment associated with it).

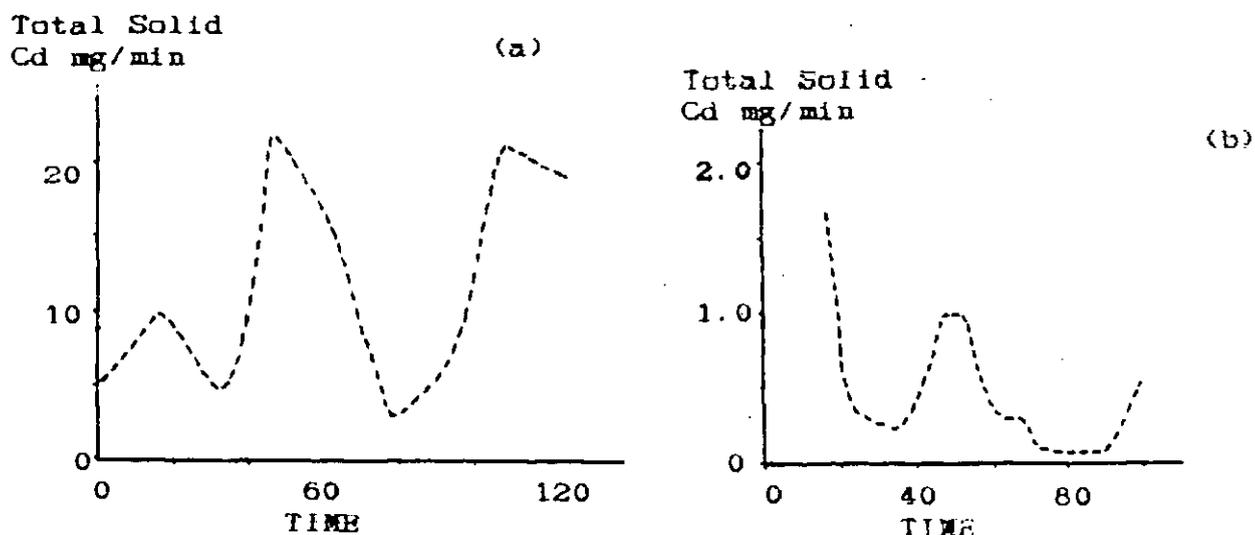


Figure 7.17 Total Solid Cadmium Loadings through two Stormwater Events.  
Time in Minutes

During the two storm events shown in Figure 7.17 the Exchangeable fraction completely dominates the profile. Storm 7A (Figure 7.2 and Figure 7.17(a)) has two primary peaks which follow suspended solid loadings, largely in the Exchangeable form. In the final late peak Cd solid loadings are unexpectedly high compared to controlling parameters. Chelex Removeable Cd loadings were also higher at this stage of the storm due to acid rain mobilisation from road dusts. During passage through the stormwater system the pH/surface area dependent solid uptake mechanism may have caused an enrichment of suspended solid Cd loadings.

A distinctive "first flush" of suspended solid Cd is seen in storm 7F (Figure 7.4 and Figure 7.17(b)). This may be due to the low flow

flushing of readily mobilised metal enriched solids. Gullypot liquor solids may be an important contribution to this early flush due to their considerable Cd enrichment (see Section 6.2.5).

Under certain conditions the Organic Cd fraction can become significant (Figure 7.18).

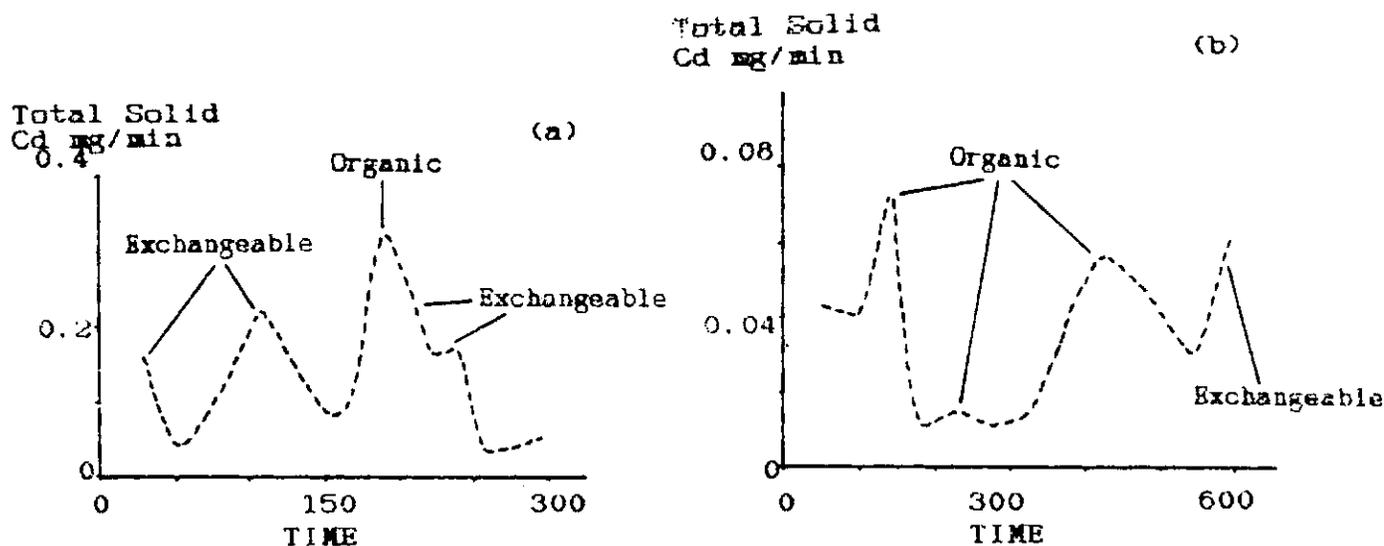


Figure 7.18 Solid Cadmium Fraction Loadings in Urban Runoff.  
Time in Minutes

In storm 7H (Figure 7.5 and Figure 7.18(a)) the first two hours of the event are dominated by the Exchangeable fraction entering from the road surface, gullypot liquor and in-pipe sediments. However, before the second flow peak an Organic Cd fraction enters. This fraction can be accounted for by gullypot basal sediment mobilisation under higher flow.

During snowmelt 7J (Figure 7.7 and Figure 7.18(b)) the continual low flow flushing of the stormwater system gives rise to Organic Cd peaks which follow flow fairly closely but are not compatible with suspended solid loadings. It may be envisaged that in the gullypot only semi-buoyant organic flocculations, perhaps with a high bacterial and Cd

content and which are at or below the gullypot water/sediment interphase, are mobilised during low flow snowmelt conditions. The Exchangeable fraction at the end of the snowmelt represents incoming snowmelt particulates from the road surface.

7.2.2.7 Suspended Solid Lead Fractions.

Generally, particulate associated Pb follows suspended solids through the hydrograph. The Exchangeable fraction usually dominates the profile and can originate from road runoff, gullypot liquor and basal sediment. In addition species transformations such as pH/surface area dependent solid uptake may contribute to the Exchangeable Pb fraction.

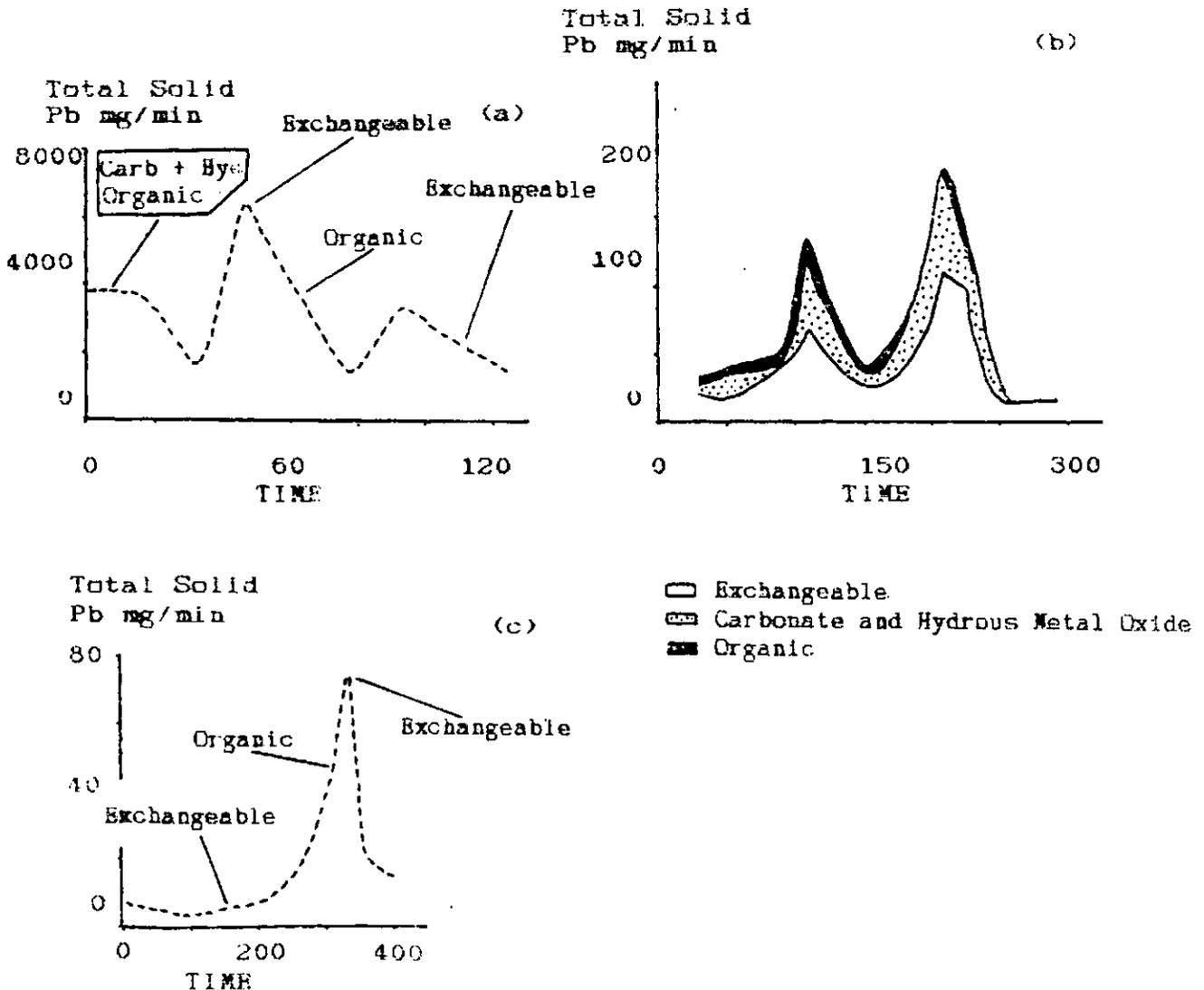


Figure 7.19 Suspended Solid Lead Fraction Loadings in Urban Runoff.

Time in Minutes

In storm 7A (Figure 7.2 and Figure 7.19(a)) a "first flush" of solid Pb containing mainly the Carbonate and Hydrous Metal Oxide, as well as the Organic, fraction occurs. The Carbonate and Hydrous Metal Oxide fraction may be derived mainly from gullypot liquor and in-pipe sediments. There is probably also a significant addition from the gullypot interstitial sediment water when the rapidly oxygenating road runoff flush oxidises Fe and Mn to their respective hydrous oxides, which in turn co-precipitate/adsorb and transport Pb. The Exchangeable fraction shows peaks with, or just before, the final two flow peaks. This represents road runoff solids and may also include mobilised gullypot basal sediment. The Organic Pb peaks are seen at the very beginning of the storm event and after the second flow peak. These may represent a gullypot product, although road runoff can also provide significant quantities of this fraction.

The Exchangeable fraction usually dominates the Pb profile and therefore it is useful to use a shaded chemograph representation as shown for storm 7H (Figure 7.5 and Figure 7.19(b)) to illustrate other contributing fractions. The Exchangeable fraction is most important throughout being indicative of road runoff and Pb enrichment at the solid surface by the action of the pH/surface area dependent solid metal uptake process (see Section 6.2.4). The Carbonate and Hydrous Metal Oxide fraction is significant throughout the storm representing gullypot product reaction and mobilisation. The most significant proportion of this fraction occurs at the beginning of the storm event when the gullypot is first mobilised and therefore represents the oxidation of reduced interstitial sediment water. This fraction is also significant for the two flow peaks which may represent the background road dust speciation. The Organic fraction is relatively unimportant, but is most concentrated in the first part of the storm. During the second flow peak less organic gullypot basal sediment may be mobilised, resulting in less Organic Pb.

During snowmelt 71 (Figure 7.6 and Figure 7.19(c)) the Exchangeable fraction dominates most of the profile suggesting the release of road sediment from melting snow. On the rising limb of the flow peak the

Organic fraction becomes important and may originate from the mobilisation of gullypot solids.

7.2.2.8 Suspended Solid Copper Fractions.

The suspended solid Cu profiles often contain all three metal fractions. The Exchangeable and Organic fractions are most representative of road runoff and gullypot liquor mobilisation. The Carbonate and Hydrrous Metal Oxide fraction indicates the effect of highly oxidising road runoff on the reduced gullypot sediment system.

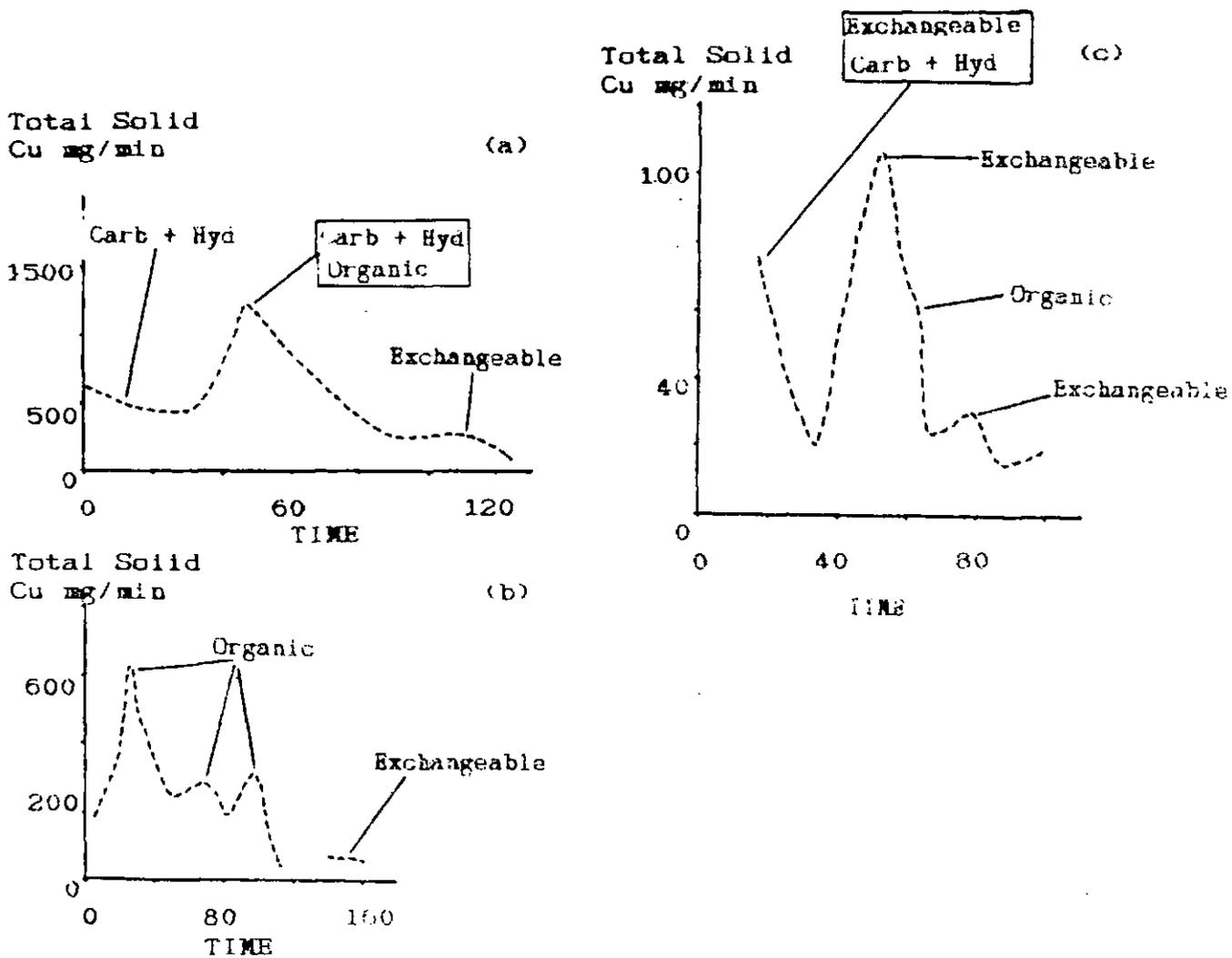


Figure 7.20 Suspended Solid Cu Loadings in Stormwater.  
Time in minutes

During storm 7A (Figure 7.2 and Figure 7.20(a)) the Carbonate and Hydrrous Metal Oxide fraction is clearly important for Cu transport

during the first half of the storm event. Fe/Mn oxidation followed by Cu co-precipitation/adsorption (as was observed for Pb) could be occurring. For significant hydrous metal oxide adsorption the pH must be greater than 5.5 for Cu and 6.0 for Pb as determined by the respective hydrolysis constants, i.e.  $p\beta_1 - 1.5$  (Table 2.9, Chapter 2). These criteria are met in the stormwater pipe during storm events. At the Oxhey site road runoff is well buffered during most of the storm event and the hydrous metal oxide formation process may well begin in the road surface water microlayer and increase significantly in the gullypot. On the Bergsjön catchment the low buffering capability of road sediments (see Section 6.2.3) means that most of the acidic rainfall buffering occurs due to the corrosion of the cement in the concrete pipes. Therefore metal uptake onto hydrous metal oxides may be largely an in-pipe process at Bergsjön. The hydrolysis constants,  $p\beta_1 - 1.5$ , for hydrous oxides (Table 2.9, Chapter 2) of 7.0 and 8.0, for Zn and Cd respectively, are not always achieved in stormwater, therefore it can be argued that hydrous metal oxide co-precipitation/adsorption is more important for Pb and Cu transport in stormwater.

Carbonates are also found in the Carbonate and Hydrous Metal Oxide fraction and, largely due to the background geology, are likely to be of importance at Oxhey but relatively insignificant at Bergsjön. Similar heavy metal uptake onto carbonate surfaces as that of hydrous metal oxides might be expected.

During storm 7A the Organic fraction shows an important peak coincident with the flow maximum. This may be a combination of road sediment and gullypot solids mobilisation, although the last Exchangeable peak, which is notably exhausted compared to flow, is probably also derived from road runoff.

In storm 7B (Figure 7.3 and Figure 7.20(b)) which followed two days after 7A, the Organic Cu fraction clearly dominates with only a small Exchangeable peak from further road dust mobilisation at the end of

the storm. Gullypot solids, particularly from gullypot liquor, may explain the multiple Organic Cu peaks. As for storm 7A the road sediments and in-pipe sediment may have become greatly exhausted. The multiple peaks can then be explained by a variable contributing area concept.

The Exchangeable fraction dominates the profile in storm 7F (Figure 7.4 and Figure 7.20(c)) and may be explained by road runoff sediments, particularly in the late stages of the storm event. The early Exchangeable and Carbonate and Hydrous Metal Oxide fraction peaks may represent enrichments of Cu due to a combination of pH/ and redox/surface area dependent metal uptake processes (see Section 6.2.4). It can be postulated that free and weakly complexed Cu, mobilised by acid rain from roofs, is rapidly adsorbed onto the surfaces of freshly formed hydrous metal oxides from the gullypots and fine road runoff solids. This reaction proceeds underground while the acidic waters are buffered by the containing concrete pipes. The Organic Cu fraction peak occurs slightly after peak flow and may be attributed to road runoff and gullypot solids mobilisation.

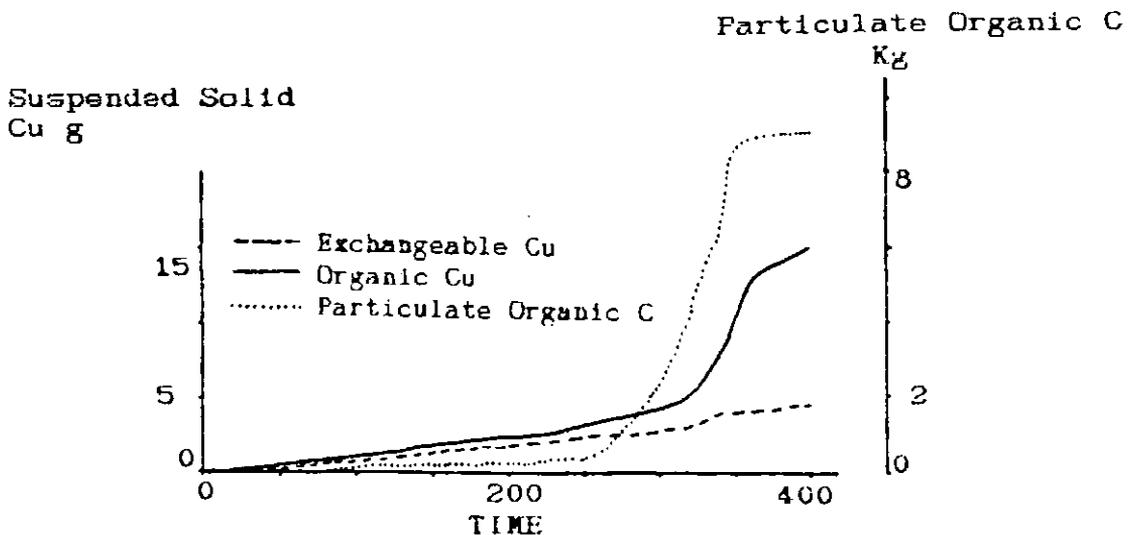


Figure 7.21 Cumulative Loadings for Suspended Solid Copper Fractions and Particulate Organic Carbon in Snowmelt.  
Time in minutes

The Organic fraction can also act as an important uptake mechanism for Cu. In snowmelt event 71 (Figure 7.6 and Figure 7.21) the cumulative loading increase of the Exchangeable fraction is gradual, while the Organic fraction increases dramatically during the light rainfall event, following the same trend as for particulate organic carbon. This can be explained by the uptake into the Organic fraction of dissolved Cu species, despite the high ionic strength. Uptake onto particulate organic materials can therefore be an important species control during snowmelt conditions, especially when high organic solid loadings overcome the solubilisation effects of ionic strength.

### 7.3 The Impact of Heavy Metals in Urban Runoff on Freshwater Life.

Two approaches have been tested for determining the potentially toxic effect of metal species in stormwater on aquatic life:

- a) Metal speciation results can be compared to Water Quality Standards to ascertain whether they are being exceeded.
- b) *Dialysis with Receiving Resins* allows an *in situ* assessment of metal transfer through a membrane and uptake by organic ligands.

#### 7.3.1 Water Quality Standards Approach.

Both EPA (EPA 1983) and EEC (Mance and O'Donnell 1983) standards have been considered with regard to potential toxic impacts on freshwater life in receiving waters (as discussed in Chapter 2) and only the proposed EPA standards take into account the impact of intermittent discharges. To allow for direct effects, as well as receiving stream dilution, the total metal EPA values can be compared to Chelex Removeable metal, i.e. free and weakly complexed metal levels, which can be considered bioavailable (Table 7.9).

Table 7.9 Percentage Time for Exceedance by Metals, of EPA Recommended Values for Intermittent Discharges, during Urban Runoff.

	% Time Exceeded during Runoff Event							
	Zinc		Cadmium		Lead		Copper	
	T.V.	S.M.	T.V.	S.M.	T.V.	S.M.	T.V.	S.M.
Storm 7A	-	-	13.3	0.7	-	-	76.5	6.5
Storm 7B	-	-	100	48.3	-	-	100	4.1
Storm 7F	-	-	4.1	-	-	-	53.4	13.3
Storm 7H	-	-	-	-	-	-	100	63.2
Snowmelt 7I	19.4	-	41.9	11.6	4.4	-	75.7	68.8
Snowmelt 7J	48.3	-	62.5	-	-	-	100	100

T.V. = Threshold Value  
 S.M. = Significant Mortality

In stormwater only Cd and Cu appear to be a significant threat to receiving water standards. Cadmium is most significant on the Oxhey catchment with considerable periods above both limits. Copper is consistently above the Threshold Limit on both catchments, although the Significant Mortality Limit is only consistently exceeded at Bergsjön. Qualitative evidence for the relevance of this exceedance is the complete absence of any observable life in the urban creek after the outfall at Bergsjön, despite high stormwater nutrient levels (Malmqvist 1983). It is realised that persistent toxic hydrocarbon and nutrient overloading could also have the same effect.

Zinc, Cu and Cd in the outfall waters exist for considerable periods above the Threshold Value in snowmelt runoff (Table 7.9). The chronic effects of these three metals are especially important for slow

snowmelt, where road salting provides a continuous release of bioavailable metal species into the drainage system. These conditions often prevail for several months in Scandinavia, but for a shorter, although sometimes significant, period in the U.K. Only during periods, when very heavy chloride concentrations in the runoff exceed 4-5 g/l, does bioavailable Pb exceed the threshold value. The significant mortality level for snowmelt is exceeded by Cd and Cu, underlining the receiving water threat from these metals.

### 7.3.2 The Dialysis with Receiving Resins Approach.

Using the *Dialysis with Receiving Resins* method (described in Chapter 5) snowmelt, baseflow and stormwater have been monitored at Bergsjön. The results, expressed as metal uptake rates, allow some indication of the rate at which metal species in stormwater could diffuse into, and be taken up by, a biological cell (Table 7.10).

A first observation is that baseflow provides a low, but significant, metal uptake. This can be attributed to the washing of in-pipe sediments by infiltrating groundwater, which has an elevated dissolved chloride level (100-200 mg Cl/l).

To understand the significance of an average 4.9 pg/mm<sup>2</sup>/hour uptake rate for Zn for baseflow a comparison with established values for biological metal uptake must be made. It is not usual for surface area to be considered in metal uptake studies (Turner 1983). However, Turner (1983) has used a value for the maximum Zn uptake flux, for the seawater alga *Phaeodactylum cornutum*, of 10<sup>-14</sup> mol/cm<sup>2</sup>/s (2.34 pg Zn/mm<sup>2</sup>/hour). In using this value diffusion is assumed to be the major metal transport mechanism across the cell membrane. As the maximum uptake flux value is already exceeded under baseflow conditions for Zn then this suggests that the washing of in-pipe sediments is already producing enough Zn to contaminate downstream organisms.

Table 7.10 *Dialysis with Receiving Resins Metal Uptake Rates for Urban Runoff.*

Period No.	Period Date	Sample	Receiving Resin	Metal Uptake Rate pg/mm <sup>2</sup> /hour			
				Zinc	Cadmium	Lead	Copper
1	24,01,85-28,01,85	Snowmelt*	Chelex	9,4	0,03	0,04	3,9
			Thiol	7,8	0,03	0,11	0,4
			Cysteine	7,8	0,16	nd	2,7
2	28,01,85-31,01,85	Snowmelt*	Cysteine	139,3	0,81	0,79	217,8
3	31,01,85-04,02,85	Snowmelt*	Chelex	20,1	0,26	0,13	6,8
			Cysteine	46,3	0,56	0,55	35,7
4	04,02,85-07,02,85	Snowmelt	Cysteine	10,6	9,5	nd	5,6
5	07,02,85-11,02,85	Snowmelt	Cysteine	12,9	5,4	0,03	1,9
6	11,02,85-14,02,85	Snowmelt	Cysteine	6,7	0,31	0,06	7,0
7	14,02,85-18,02,85	Snowmelt	Cysteine	12,7	0,64	0,19	1,2
8	18,02,85-21,02,85	Snowmelt*	Cysteine	2,7	nd	nd	0,4
9	21,02,85-25,02,85	Snowmelt*	Cysteine	17,1	0,53	0,25	27,2
10	25,02,85-28,02,85	Snowmelt*	Cysteine	16,8	0,68	nd	13,8
11	28,02,85-04,03,85	Snowmelt*	Cysteine	20,9	5,2	0,33	30,0
12	10,05,85-14,05,85	Baseflow	Cysteine	4,2	0,03	0,3	5,9
13	18,05,85-21,05,85	Baseflow	Cysteine	5,5	nd	0,05	2,8
14	24,05,85-28,05,85	Stormwater	Cysteine	38,8	0,09	0,24	10,2

\*Significant Snowmelt

\*Sporadic Snowmelt

nd = not detected

The stormwater discharge, representing an 8 mm rainfall depth, has the effect of increasing metal uptake for Zn, Cd and Cu, and possibly Zn.

Certain heavy snowmelt periods increase metal uptake greatly. The heaviest melt was during Period 2, which is reflected in the high metal concentrations found for the sampled period (snowmelt 7I), and for the *Dialysis with Receiving Resins* results.

After Period 3 there was a cold two week period ( $\approx -10^{\circ}\text{C}$  to  $-20^{\circ}\text{C}$ ) with little snowmelt, but continued baseflow (from groundwater infiltration). The results over this period (Table 7.10) show that it

is several days before a low uptake rate is reached. This can be attributed to the continual washing of in-pipe sediments by baseflow. These sediments have been deposited in the pipe after the snowmelt event and clearly represent a significant bioavailable metal source.

During Periods 1 and 3 a comparison was made between the metal uptake rates for resins containing different complexing ligands. The Chelex-100 and cysteine resins removed metals at similar rates during Period 1, except for Cd which was more readily taken up by the cysteine resin. In Period 3 the cysteine resin removed all four metals at a greater rate than Chelex-100. The Thiol resin had a lower removal rate than either cysteine or Chelex-100 resins for Cd and Cu, but a similar rate for Zn and a higher rate for Pb.

Table 7.10 also shows that Cd uptake is consistently as high, often higher, than Pb, despite a total Pb concentration in urban runoff of 100-1000 times greater than Cd. These results confirm the speciation scheme results which show that Pb is usually predominantly particulate associated and therefore unable to enter the cell membrane.

Alternatively, Pb is consistently associated with the Strongly Bound fraction which may not react with cell constituents. Zinc and Cd are often in soluble bioavailable forms and therefore show significant uptake by *Dialysis with Receiving Resins*.

## CHAPTER 8 CONCLUSIONS AND RECOMMENDATIONS.

### 8.1 Summary of Findings.

a) A comprehensive review of the relevant literature has enabled the formulation of a practical and manageable metal speciation scheme which allows the bioavailability and geochemical mobility of metal fractions in stormwater to be ascertained. The operationally defined dissolved phase was separated into fractions related to the relative complexation strength, while the suspended solid phase was fractionated according to the relative ease of release of the metals.

b) *Dialysis with Receiving Resins* has been developed as an alternative method for the analysis of metal uptake rates in stormwater and snowmelt. The technique involves encapsulating a cysteine resin in a dialysis bag and the measured metal uptake rates, onto the resin, allow an interpretation of the potential impact of bioavailable metal species on the biota of receiving waters.

c) Six important processes have been identified which contribute to or affect the transport of heavy metals through a gullypot system.

- i) Atmospheric Fallout
- ii) Acid Rain Mobilisation
- iii) Free and Weakly Complexed Metal Ion Reaction.
- iv) pH/Surface Area Dependent Suspended Solid Metal Transport
- v) Metal Increase in the Gullypot Liquor between Storm Events
- vi) Gullypot Liquor and Sediment Contribution to Metals in the Gullypot Outflow

d) Gullypot metal fraction loadings through the gullypot system were found to reflect the mobilisation processes and species transformations occurring within the system. Individual metal species indicate the mobilisation of different parts of the gullypot system and speciation changes therein.

e) Mass balances for metals and metal fractions in the gullypot system show that dissolved metal species are rapidly washed through the system with the rate of the washoff of road sediment bound metal being greatly increased by acid rain mobilisation. The gullypot liquor and interstitial sediment water are washed out of the gullypot early in the storm event and are highly enriched in metals, which have been released from maturing basal sediments between storm events. As a consequence of the physical mobilisation of gullypot basal sediment, and the associated metals, gullypot derived solid pollutants may become significant during heavy thunderstorms.

f) Separately sewered stormwater runoff, sampled at sites in Sweden and the U.K. is found to contain significant concentrations and loadings of Zn, Cd, Pb and Cu. Bioavailable forms (Electrochemically Available/Chelex Removeable + Exchangeable) represent 68% of the Zn, 76% of the Cd, 66% of the Pb and 32% of the Cu. Dissolved bioavailable metal loadings are greatly increased during snowmelt conditions due to the removal of solid associated metal species by the high dissolved chloride concentrations (1-17 g/l). Copper loadings are higher at the Swedish site due to the use of this metal as a construction material.

g) Measurements of the individual metal species at the stormwater outfalls show that these load at different rates onto the chemographs. The loading rate variations can be explained in terms of controlling parameter concentrations, as well as the influence of mobilisation and transport processes, as described in (c). Bioavailable Chelex Removeable metal peaks often appear late in the hydrograph, due to the acid rain mobilisation of road sediments, which provides a prolonged water quality impact for the receiving waters when the dilution capacity is decreasing. Interstitial sediment water and gullypot liquor dissolved metal species are usually washed out of the gullypot early in storm events and show a close relationship to variations in conductivity.

h) A comparison of the observed bioavailable metal concentrations has been made with EPA Water Quality Standards. For stormwater, Cd and Cu

were found to be a significant threat to receiving water quality objectives. Snowmelt runoff presented a considerable water quality threat in terms of Zn, Cd and Cu, as a direct result of road salting practice. Zinc, Cd and Cu accumulated significantly during *Dialysis with Receiving Resins* tests for both stormwater and snowmelt. Cadmium, which is present in stormwater at 100-1000 times lower total concentration than Pb, shows a similar uptake rate. This reflects the importance of speciation studies for identifying bioavailable metal species.

### 8.2 Implications for Stormwater Quality Control.

The findings of this study have provided useful guidelines to evaluate alternative municipal practices for the reduction of potentially harmful effects of priority metals contained in urban runoff on receiving waters.

In the long term the introduction of porous pavements and verge soakaways, as well as stormwater storage and treatment facilities, such as detention and lagoons, would provide a substantial reduction of metal loadings in urban runoff (Hall and Ellis 1985, Perry and McIntyre 1985). However, the implementation of these management alternatives require relatively high capital and management costs. In addition the inefficiency of conventional storage and treatment facilities for the reduction of toxic dissolved metal species should not be overlooked, especially if cost-effective objectives are to be met.

In the short term an optimisation of the frequency of gullypot cleaning, road dust sweeping and dry weather storm sewer flushing would greatly improve the quality of stormwater runoff, in terms of reducing the amount of metal (as well as solids, hydrocarbons and Biological Oxygen Demand) available for remobilisation and washout. In particular the control of road sediment metal loadings would greatly reduce the amount of metal which can be removed by acid rain

mobilisation processes and therefore reduce the concentrations of bioavailable Chelex Removeable metal in stormwater runoff. This study has shown that the rapid accumulation and subsequent washout of metals through the storm drainage system would require frequent road surface and storm pipe cleansing procedures on a four to seven day cycle to limit pollution from these sources.

In addition to stepping-up these already well established engineering practices, restrictions on automobile parking would be a relevant environmental procedure. Automobiles provide the most significant non-point source of heavy metal loadings to road dusts. Therefore, parking controls and traffic restrictions in selected areas where the storm drainage enters particularly sensitive receiving streams or lakes could give rise to considerable improvements in water quality.

During the winter season, especially in countries with a long winter such as Sweden, unnecessarily heavy road salting should be avoided, as it can lead to highly elevated bioavailable metal runoff concentrations by assisting the solubilisation process. A reduction of road salting to 25% of present levels would give an estimated decrease in soluble bioavailable concentration of 60% for Cd, 80% for Cu and 63% for Zn. The receiving water biota would also gain the additional benefit from a reduction of osmotic stress brought on by the high ionic strength imposed by snowmelt runoff.

### 8.3 Indications for Future Research.

a) This study has shown that gullypot sediments and their interstitial waters undergo chemical and biological changes during storm events. The effect and significance of changes in controlling parameters such as redox potential, conductivity and dissolved oxygen concentration in affecting metal speciation changes need to be analysed in more detail, to provide a fuller understanding of these interactions. This might lead to a fuller understanding of the processes occurring at the interstitial water/sediment interface which affect gullypot metal speciation.

b) Roof runoff has not been considered in any detail in this study. However, it is known that high concentrations of Cu exist in roof runoff at the Bergsjön site due to acid rain washing. The study of speciation changes, for roof runoff derived metals, which occur on contact with relatively buffered subsurface stormwater should be of interest. In addition, the overall relative contribution of road runoff to the receiving water toxicity levels (in comparison to road surface contributions) needs to be established. The timing of roof inputs could be of some significance in both water quality and management terms.

c) The role of in-pipe sediments in contributing metal species to urban runoff is an area which has not yet been investigated. This would greatly assist in obtaining an understanding of the metal speciation processes throughout the complete stormwater system. The *Dialysis with Receiving Resins* results suggest that in-pipe sedimentary metal may be released into infiltrating baseflow and into dry weather flows and this might represent a chronic toxicity threat to receiving waters.

d) The preliminary work described in this thesis concerning the use of the *Dialysis with Receiving Resins* method indicates that this requires further investigation and development. The versatility of this method can be tested by a laboratory based study of the uptake efficiency of different metal species under varying controlling parameter conditions. This would aid in the interpretation of data for metal uptake rates in urban runoff and receiving waters. The resin method could be further extended to a study on the more persistent hydrocarbons, such as benzo(a)pyrene, by the use of Amberlite XAD-2 as a receiving resin.

e) The ultimate fate of the heavy metal species carried by urban runoff will to a great extent depend on speciation changes following contact with the receiving waters. Mixing experiments (Sholkovitz 1976) between samples of urban runoff and receiving waters would

determine whether soluble bioavailable species remain in a potentially toxic state.

f) An interdisciplinary study is required to determine the most cost-effective methods for reducing the concentrations and loadings of bioavailable metal species in stormwater, both in terms of short and long term water quality objectives. This could include an evaluation of the performance and efficiency of various source control methods and of variations in gullypot and inlet design.

g) There is a need to combine chemical metal speciation data with biological monitoring to define the relative metal species "sensitivity" of differing aquatic fauna. By further comparing the biological uptake response with the *Dialysis with Receiving Resins* method a full evaluation of the newly developed method could be made.

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## APPENDIX.

The appendix contains the following papers published in international journals or presented at international conferences:

- A. Heavy Metal Partitioning between the Dissolved and Suspended Solid Phases of Stormwater Runoff from a Residential Area. *The Science of the Total Environment*, 33, 287, (1984).
- B. Variations of Dissolved and Suspended Solid Heavy Metals through an Urban Hydrograph. *Environmental Technology Letters*, 7, 313-318, (1984).
- C. The Physico-Chemical Speciation of Zinc, Cadmium, Lead and Copper in Urban Stormwater. In: Balmér, P., Malmqvist, P., Sjöberg, A. (eds.), *Planning and Control of Urban Storm Drainage*, 989-1000. Chalmers University of Technology, Gothenburg, Sweden. (1984).
- D. The Transport Mechanisms, Phase Interactions and Effects of Heavy Metals in Snowmelt Runoff. In: Vernier, J.P. (ed), *Interactions between Sediments and Water*, 226-229, CEP Consultants Ltd., Edinburgh. (1984).
- E. The Transport Mechanisms and Phase Interactions of Bioavailable Heavy Metals in Snowmelt Runoff. *Journal of Environmental Geology and Water Science*. In Press.
- F. A Physico-Chemical Speciation Scheme for the Analysis of Cadmium, Copper, Lead and Zinc in Urban Stormwater Runoff. Poster Contribution to the 30th International Congress of Pure and Applied Chemistry. (1985).
- G. The Continuous On-Line Monitoring of Environmental Pollutants in Stormwater. *Vatten*, 41, 91-96. (1985).

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HEAVY METAL PARTITIONING BETWEEN THE DISSOLVED AND SUSPENDED  
SOLID PHASES OF STORMWATER RUNOFF FROM A RESIDENTIAL AREA.

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Highway surface sediments and their associated heavy metals may be rapidly mobilised during rainfall activity and washed to receiving waters. Stormwater solids contain predominantly fine particles which are generally enriched with heavy metals. Consequently total metal levels in the suspended solid phase of urban runoff are generally higher than in corresponding street surface sediments. The dissolved phase of urban runoff waters has been shown to contain between 5% and 50% of the total heavy metals with cadmium in particular being very soluble in road runoff.

This paper considers the variation in the distribution of Cd, Cu, Pb and Zn between the soluble and particulate phases of runoff samples collected throughout two consecutive storms over the period 24 February to 2 March 1983. The catchment area is a 247ha housing estate located in the outer fringes of N.W. London. Samples were collected at 7.7 min. intervals during each storm and were separated into dissolved and suspended phases by filtration through 0.4  $\mu$ m polycarbonate filters. Following acid extraction of each fraction the metals were analysed by Differential Pulse Anodic Stripping Voltammetry.

Cd, Cu and Zn in the runoff from both storms are found to be present mainly in the dissolved phase whereas Pb is most strongly associated with the suspended solid phase. The proportion of all metals becomes quite significant towards the end of the second storm. The patterns of flow-weighted metal loadings during the storms indicate that Cu, Pb and Zn are mainly derived from road runoff whereas the aberrant behaviour of Cd suggests another source or combination of sources.

## VARIATIONS OF DISSOLVED AND SUSPENDED SOLID HEAVY METALS THROUGH AN URBAN HYDROGRAPH

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### ABSTRACT

Zn, Cd and Cu in stormwater runoff from an urban catchment are found to be present mainly in the dissolved phase, whereas Pb is most strongly associated with the suspended solid phase. High levels of metals, particularly Cu, are found in stormwater solids which may be due to the high percentage of particulate organic material in the runoff. The metal loadings over the storm event for the dissolved and suspended solid associated metals show similar distributions to the flow and suspended solids respectively. However, in some cases secondary peaks and deviations due to dissolved metal scavenging are observed.

### INTRODUCTION

Highway surface sediments often contain elevated levels of heavy metals which are rapidly mobilised during rainfall activity and washed into receiving waters (1,2). The associated outfalls to the urban runoff, which often drain relatively large catchments, exert a considerable heavy metal flux locally on the receiving stream.

Runoff volume, land use and antecedent dry period length have been identified as regulating these pulses of heavy metals (3), although dilution-exhaustion may occur where the supply of heavy metals is limited by initial availability. Other limiting factors may be where differing sub-catchments load onto the storm hydrograph at different times, or where a transport limited situation arises.

The two main inputs of heavy metals to highway surfaces are from atmospheric and vehicular sources. Rainwater can contribute significant quantities of heavy metals and may also sparge, leach and flush the highway surface (4). The heavy metals on the road surface, mostly derived from vehicular emissions, are largely adsorbed onto or associated with highway particulates (5).

Heavy metals in urban runoff waters may be strongly attracted to the suspended solid phase (6-9) with good correlations existing between suspended solids and heavy metals. Fine particles predominate in stormwater solids (4) and these particles are generally enriched with heavy

metals (2,10). Consequently total heavy metal levels in stormwater solids are generally higher than in corresponding raw street sediments (11,12).

This paper discusses concentrations, loadings and temporal distribution patterns of heavy metals in urban runoff, and is part of a larger study being undertaken of these problems (13,14).

## EXPERIMENTAL

Stormwater samples from two storms were collected at the major outfall of a 214 ha semi-detached housing estate catchment located in the outer fringes of NW London. 500ml polyethylene bottles, which had been washed successively with chromic acid and nitric acid (10%), were placed in an automatic sampler and samples collected at intervals of 7.7 minutes after the flow rate had reached 91 litres sec<sup>-1</sup>. The samples were stored in a refrigerator at 4°C and 23 alternate samples from two storms covering the period 24 February to 2 March 1983 were analysed.

The dissolved and suspended solid phases of the stormwater were separated by filtration through 0.4 µm Nucleopore polycarbonate filters, using a polyethylene Millipore filtration system. After filtration the suspended solid phase was air dried (50°C) and the dissolved phase stored at 4°C.

The concentrations of suspended solids were determined gravimetrically, whilst dissolved organic carbon was quantified using an Ionics 1258 Organic Carbon Analyser. Dissolved chloride was determined spectrophotometrically, after the addition of mercuric thiocyanate, using a Technicon Auto-Analyser.

Analysis of Zn, Cd, Pb and Cu was carried out using a Princeton Model 384 Polarographic Analyser in the Differential Pulse Anodic Stripping Voltammetry (DPASV) mode.

To release the soluble metals, an oxidising mixture of concentrated nitric acid (0.18 ml) and concentrated perchloric acid (0.02 ml) was added to an aliquot of the dissolved phase (25 ml). The mixture was heated on a sand bath and after evaporation to dryness the residue was taken up in 1M HNO<sub>3</sub> (10ml). Following dilution to 25 ml the metal levels in an aliquot (7 ml) were determined after the addition of 2M sodium acetate buffer solution (3 ml).

The particulate associated metals were digested with concentrated nitric acid (18 ml) and concentrated perchloric acid (2 ml) to extract the metals. The resulting extract was evaporated to dryness and the metals taken up in 1M HNO<sub>3</sub> (10 ml). The solids were washed with double distilled deionised water (10 ml) and the supernatants combined. The metal levels in an aliquot (7 ml), from a total volume of 25 ml, were determined by DPASV after the addition of 2M sodium acetate (3 ml).

The precision of the analysis was better than ±10% for the suspended solid associated metals and better than ±25% for the soluble metals.

## RESULTS AND DISCUSSION

The total loadings and average concentrations of heavy metals over both storms (Table 1) show that much higher loadings of Zn and Cd occur as dissolved, as distinct from particulate, metal. Cu is distributed fairly evenly between both phases while Pb is predominantly particulate associated. The preference for the dissolved phase compared to the suspended solid phase is in the order: Zn > Cd > Cu > Pb.

Zn, Pb and Cu, in both the suspended solid and dissolved phases, show similar average concentrations during both storms suggesting that

TABLE 1: Loadings and average concentrations of heavy metals in storms 1 and 2

	Storm 1				Storm 2			
	Zn	Cd	Pb	Cu	Zn	Cd	Pb	Cu
LOADINGS								
DISSOLVED (g)	212.5	2.7	16.4	52.9	195.2	10.6	21.5	57.3
SUSPENDED SOLID (g)	72.1	1.4	367.3	63.8	37.9	3.7	140.9	36.0
CONCENTRATIONS								
DISSOLVED ( $\mu\text{g l}^{-1}$ )	227.4	3.4	17.0	53.8	162.8	9.1	17.8	47.2
SUSPENDED SOLID ( $\mu\text{g g}^{-1}$ )	413.9	11.5	2464.4	413.6	551.6	60.3	1910.7	481.6

TABLE 2: Relevant parameters for storms 1 and 2

	Storm 1	Storm 2
pH range	7.1 - 7.6	7.2 - 7.6
Total flow $\text{m}^3$	993	1252
Total suspended solids loading (kg)	165.2	67.0
Dissolved organic carbon loading (kg)	8.3	8.1
Dissolved chloride loading (kg)	55.4	9.4

a similar source material or input is contributing. Similarities between the particulate metal levels and those in typical road surface sediments (15) indicate that road surface runoff is the principal source of Zn, Cu and Pb for both storms. The elevated particulate Cu concentrations can be partly attributed to the finer nature of storm-water suspended solids which are characteristically less than 25  $\mu\text{m}$  (16) and also to their higher organic carbon content (20-30%). Cd shows greatly elevated levels in the second storm compared to the first, suggesting a distinctive or separate contributing source material.

The distribution of all metals between the soluble and particulate phases is similar for both storms. The controlling parameters for the partitioning of heavy metals between the dissolved and suspended solid phases include pH, flow, suspended solid concentrations, dissolved organic carbon and dissolved chloride concentrations. The pH ranges are almost identical and there is little difference in the total flow or the dissolved organic carbon loadings for either storm (Table 2). The major differences are the greater suspended solid loadings and dissolved chloride loadings in storm 1. This storm was preceded by several weeks of dry weather allowing the accumulation of surface sediments, while only two days elapsed before a further flushing occurred to generate storm 2. The accumulation-limited conditions, although lowering the loadings of suspended solid associated Zn, Pb and Cu in storm 2, do not seriously affect the phase distribution of the metals. This is also true of the dissolved chloride which shows a more significant dilution-exhaustion response in the second storm.

The variations of flow-weighted heavy metal loadings between the dissolved and suspended solid phases are illustrated in Figure 1. The proportion of all metals in the dissolved phase increases as both storms progress and for Pb the dissolved phase becomes quite significant towards the end of the second storm. The changes observed in the dissolved organic carbon and the dissolved chloride throughout the storms cannot on their own account for the dissolved-suspended solid interactions. A more probable interpretation is the increase over the storm of the water-sediment ratio which results in less suspended solid adsorption of heavy metals.

The flow-weighted loadings of suspended solid associated metals, as represented for Zn in Figure 2, generally show a similar pattern to that of suspended solids for storm 1. However, Cu does not show the first peak which may be related to the combined effects of high ionic strength and dissolved organic carbon altering the equilibrium in favour of the dissolved form compared to solid associated metal. During storm 2 Pb follows suspended solids exactly with Cd showing a pronounced first flush. However, Cu, Zn and Cd show secondary and late flushes suggesting a retarded input of suspended solids enriched with these metals.

The late flushes of suspended solid associated metals in storm 2 (illustrated in Figure 2 for Zn) may be accounted for by a variable contributing areas concept. These metals have taken longer to arrive from their source, either due to a different rate of mobilisation, or because of a longer travelling distance. These reasons may be further complicated by variations in rainfall intensity and by in line sewer mixing processes.

The flow-weighted loadings of all four dissolved metals throughout storm 1 show similar trends. Although there is an obvious second peak, which is related to flow (Figures 1 and 2), there is no initial peak. This is probably because a flux of dissolved metals may take some time to be mobilised or require a high rainfall intensity threshold. Another explanation may be that the dissolved metals are scavenged by the suspended solid phase. All the metals show an increase in loading near the end of the storm which may relate to the corresponding increase observed for dissolved organic carbon and dissolved chloride. For the

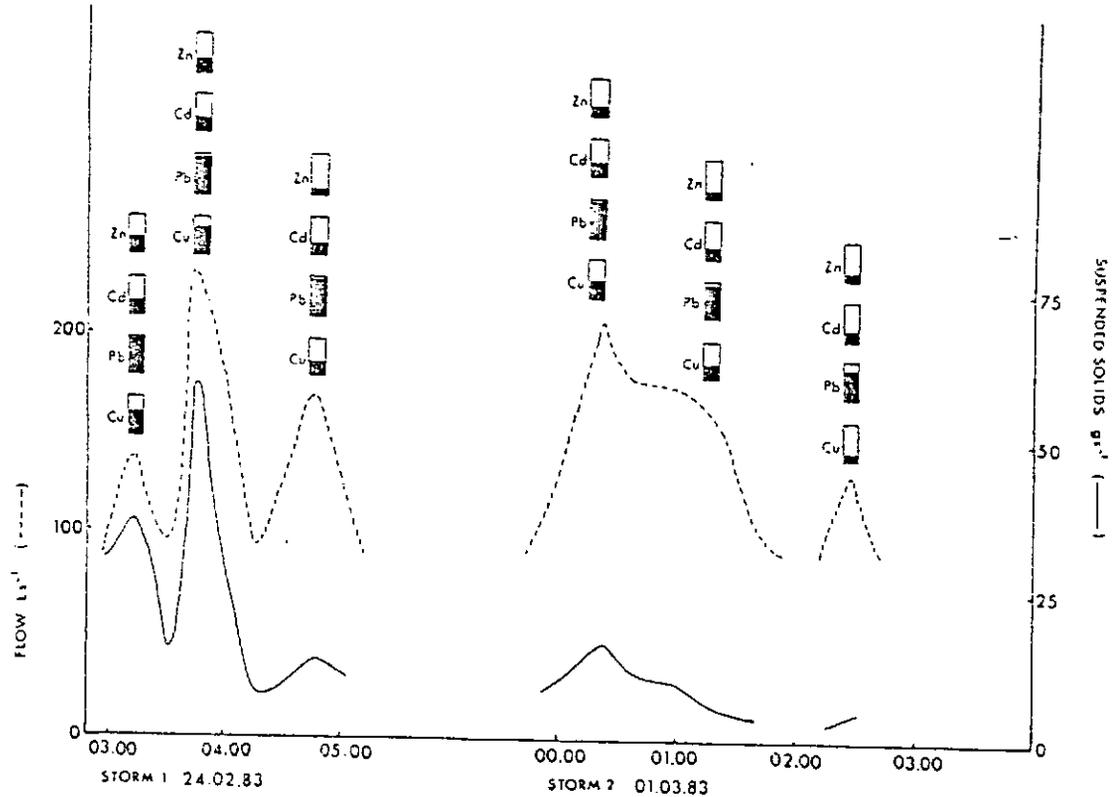


FIGURE 1 RELATIVE PERCENTAGES OF THE DISSOLVED AND SUSPENDED SOLID PHASES FOR EACH METAL. THE SUSPENDED SOLID PHASE IS SHADED.

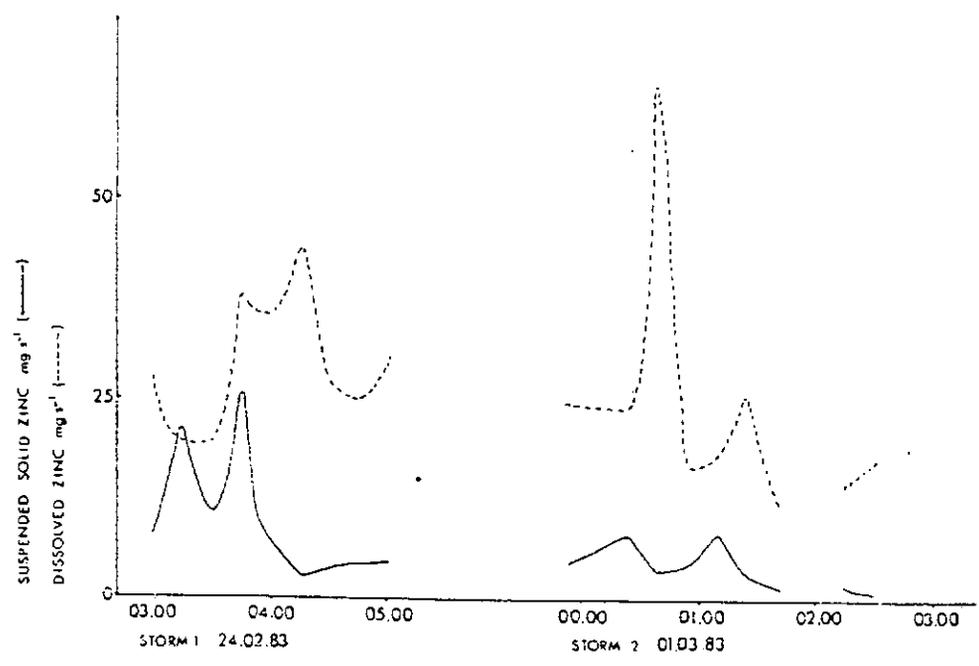


FIGURE 2 FLOW-WEIGHTED LOADINGS FOR ZINC IN THE DISSOLVED AND SUSPENDED SOLID PHASES.

dissolved phase of storm 2 the initial peak only follows flow in the case of Cd, while the other metals show a lag behind the peak flow (Figures 1 and 2). A secondary peak is observed for all the metals, reflecting similar anomalous peaks which were also present for metals in the suspended solid phase.

In both the suspended solid and dissolved phases Cd flow-weighted loadings generally follow flow accurately but greater loadings occur in storm 2 (Table 1). These increased Cd levels may be due to a combination of different sources and rates of mobility. This also suggests that Cd levels are not controlled by the same mechanisms as Zn, Pb and Cu.

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# The Physico-Chemical Speciation of Zinc, Cadmium, Lead and Copper in Urban Stormwater

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## ABSTRACT

A physico-chemical speciation scheme has been applied to the analysis of zinc, cadmium, lead and copper in stormwater samples collected from selected urban catchments in England and Sweden. Zinc and cadmium exhibit a preference for the dissolved phase whereas lead predominates in the suspended solid phase. Copper is distributed equally between both phases.

The potentially toxic forms of the metals in the dissolved phase (Electrochemically Available) and in the particulate phase (Exchangeable) account for 63% of the total zinc, 77% of the total cadmium, 66% of the total lead and 32% of the total copper. The Exchangeable fraction of the suspended solid phase exhibits unexpectedly high metal levels which may be easily released on contact with receiving waters and thus provide a major source of bioavailable metals.

Both UK and Swedish catchments show consistently similar distributions of all four metals between the six experimentally determined fractions. The major differences are the higher lead concentrations found at the UK site and the considerably larger copper concentrations which are distinctive of the Swedish catchment. These higher copper levels accompany a free or weakly complexed copper contribution to the soluble phase which is absent within the UK catchment.

Keywords: physico-chemical metal speciation, stormwater pollution, bioavailability, heavy metals, concentrations, loadings.

## INTRODUCTION

Polluted urban surface runoff may have a serious impact on sensitive receiving waters, the occurrence of heavy metals in unacceptably high concentrations is a particular cause for concern (Randall et al. 1978, Wilber and Hunter 1979, Malmqvist 1983).

Earlier studies on urban runoff analysed total heavy metal concentrations or loadings as an index of stormwater toxicity. It was believed that the greater proportion of metals were suspended solid associated (Mance 1981). We have shown that for zinc, cadmium and copper the dissolved phase may be equal to or greater than the particulate phase (Morrison et al. 1984). The available evidence strongly indicates that the free dissolved or weakly associated suspended solid metal forms are bioavailable, and thus also potentially toxic to receiving water biota (Theis and Dodge 1979, Sunda and Gillespie 1979, Tessier et al. 1979, Guy and Kean 1980, Salomons and Forstner 1980, Petersen 1982, Florence et al. 1983). No detailed separation of the bioavailable and non-bioavailable metal species in stormwater has yet been attempted.

A speciation scheme has recently been devised which allows a separation of bioavailable and non-bioavailable heavy metal species (Morrison 1983). This differs from previous schematic applications to natural waters (Batley and Florence 1976, Laxen and Harrison 1981) and sediments (Gibbs 1973, Tessier et al. 1979, Salomons and Forstner 1980) in providing a more rapid and experimentally straightforward evaluation of the toxic fractions.

This paper discusses the application of the scheme to stormwater runoff quality within urban catchments in both England and Sweden.

## CATCHMENT CHARACTERISTICS AND EXPERIMENTAL METHODS

### Catchment Characteristics

The UK catchment is a 214 hectare, 18% impervious, residential catchment situated in the outer north west fringes of Metropolitan London. Early studies have been described in detail by Wilkinson (1956). The catchment drains to a trapezoidal flume and flow is recorded by a potentiometric level meter at one minute intervals on a data logger. Sampling was carried out automatically at seven minute intervals.

The Swedish catchment is a 15.4 hectare, 42% impervious, multi-storey residential catchment in Göteborg, Sweden. The Bergsjön area has been studied by Årnell (1980). Flow is continuously monitored using an ultrasonic level meter at a V-notched weir situated at the outfall to the catchment. Flow-weighted sampling is carried out automatically at the commencement of each storm event.

### Experimental Methods

Field samples were collected in 1 litre polyethylene bottles at both sampling stations. The stormwater samples were then immediately returned to the laboratory. All filtration was carried out on the sampling day.

An aliquot of each sample (250 mls:) was set aside for the determination of pH, dissolved chloride and organic carbon. A further aliquot (250 mls.) was analysed for heavy metals according to the speciation scheme illustrated in Figure 1 and which is described in detail elsewhere (Morrison 1983).

The precision of the schematic analysis has been tested for each fraction. For all metals, the precision for each of the dissolved metal fractions is always better than  $\pm 25\%$  and generally better than  $\pm 10\%$ . For the suspended solid phase the precision is better than  $\pm 10\%$  in all three fractions.

### Interpretation of the Speciation Scheme

The dissolved and suspended solid phases were operationally defined by filtration through a 0.4  $\mu\text{m}$  Nucleopore polycarbonate filter. The dissolved phase is separated into three fractions, depending on the complexation strength of the heavy metals.

#### 1. Electrochemically Available Fraction

The free ions and weakly complexed metals were determined by Anodic Stripping Voltametry. This fraction can be compared to the bioavailable metal as defined by Whitfield and Turner (1979).

#### 2. Chelex Removeable Fraction

Batch extraction with Chelex-100, a metal selective ion exchange resin, removes those metals associated with the Electrochemically Available fraction as well as more strongly bound metals but does not retain soluble metals which are strongly bound to colloids or complexes Figura and Mc Duffie (1979). Florence et al. (1983) have shown that this fraction may over-estimate the truly bioavailable metal but it does give an indication of those metals attached to ligands by a medium complexation strength.

#### 3. Strongly Bound Fraction

The Strongly Bound Fraction has been defined as the difference between the total dissolved metals and the Chelex Removeable Fraction. The experimental conditions used to determine this fraction indicate the strong association of the metals as complexes or colloids and ensure that they may be considered non-bioavailable as far as receiving water biota is concerned.

The suspended solid phase was divided into three fractions according to the ease of metal release.

#### 4. Exchangeable Fraction

Particulate associated heavy metals which exchange or complex with anions may be released into the soluble phase under normal pH conditions in stormwater. This solubilisation process is particularly probable under the high chloride concentrations which are often encountered in urban runoff (see Table 1 in the Results and Discussion section).

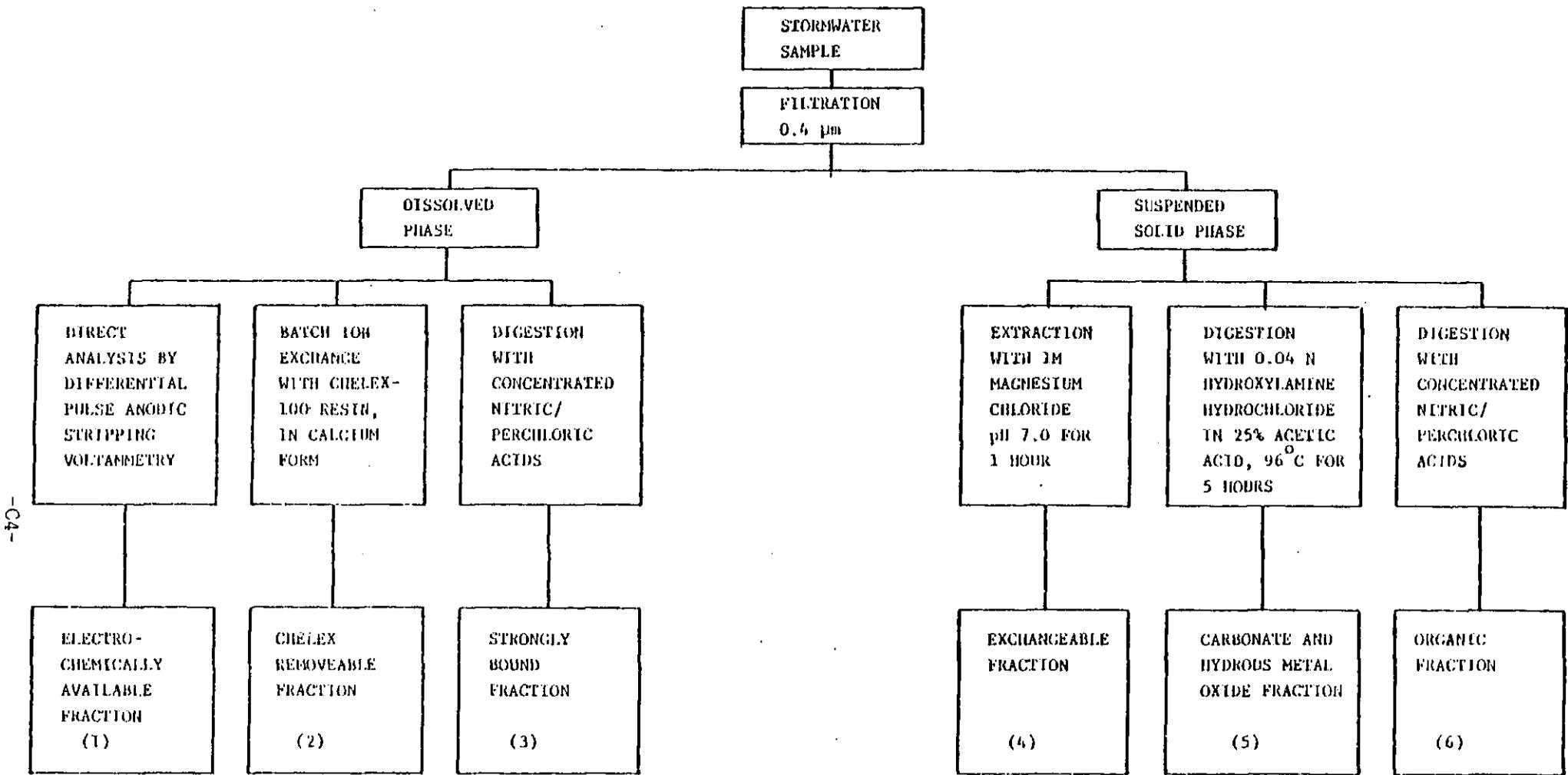


Figure 1. The scheme of analysis for heavy metal speciation.

-C4-

## 5. Carbonate and Hydrous Metal Oxide Fraction

The metals in this fraction are more strongly bound than the Exchangeable fraction and occur mainly as surface associated metals (Davis and Leckie 1978) and co-precipitates of hydrous metal oxides and carbonates. This fraction is unlikely to have any immediate biological impact on the receiving waters, but may accumulate in river or estuarine sediments. Subsequently the metals may be released into the water column when a significant drop in pH occurs (Florence and Batley 1980).

## 6. Organic Fraction

The remaining metals are largely organically bound in polluted suspended solids or sediments (Morrison 1983) and because of their strong association are unlikely to be bioavailable. However, this fraction may act as an important transportation mechanism and sink for such metals as lead and copper, which have high stability constants with organic compounds (Mantoura et al. 1978).

# RESULTS AND DISCUSSION

## Concentration Averages and Loadings

The average concentrations for each metal fraction and for all the storm events are given in Table 1.

The zinc and cadmium concentrations are similar for both catchments, while the lead concentrations are 2 to 4 times higher in the UK catchment. The copper concentrations are nearly an order of magnitude greater within the Swedish catchment. This is most certainly due to the use of copper roofing and guttering in Sweden (Malmqvist and Svensson 1977), which is not a common practice in the UK.

The dissolved concentrations for all metals are generally high. The concentration of the dissolved metal will be determined by solubility, pH, ionic strength, dissolved organic ligands and the flow/suspended solids ratio (Morrison et al. 1984). Overall, the levels of dissolved metals in stormwater are significantly higher than those quoted for rivers or seawaters (Florence and Batley 1980).

The suspended solid concentrations are greater than those associated with typical road dusts, particularly in the case of cadmium and copper (Hamilton et al. 1984). To a large extent this enhancement is explained by the fine, highly organic nature (~20%, as shown in Table 1) of stormwater solids. This ensures a high surface area and the availability to the metals of many organic complexing sites.

The loadings (Table 2) demonstrate the magnitude of the four metals discharging from both catchments. The loadings of the bioavailable forms of all four metals are significant and may have a deleterious effect on the biota of receiving waters which must prejudice long term quality objectives and user standards.

Table 1. Average Concentrations for the Heavy Metal Fractions and Parameters during each Storm Event.

			STORM EVENT			
			OXHEY 830224	OXHEY 830602	BERGSJÓN 831004	BERGSJÓN 831027
ZINC	Dissolved $\mu\text{g l}^{-1}$	Electrochemically Available	99.4	57.1	118.3	72.2
		Chelex Removeable	128.5	77.4	110.8	77.6
		Strongly Bound	55.3	14.6	91.5	13.6
	Suspended Solid $\mu\text{g g}^{-1}$	Exchangeable Carbonate and Hydrous Metal Oxide	258.1	477.1	202.1	547.7
		Organic	43.6	50.5	37.7	159.2
			160.3	242.2	32.4	237.8
CADMIUM	Dissolved $\mu\text{g l}^{-1}$	Electrochemically Available	3.6	2.4	2.7	0.6
		Chelex Removeable	4.8	2.5	2.3	1.0
		Strongly Bound	1.3	0.2	0.6	0.4
	Suspended Solid $\mu\text{g g}^{-1}$	Exchangeable Carbonate and Hydrous Metal Oxide	30.3	9.1	7.2	3.1
		Organic	5.1	n.d.	n.d.	1.2
			n.d.	n.d.	n.d.	0.3
LEAD	Dissolved $\mu\text{g l}^{-1}$	Electrochemically Available	6.6	5.6	3.2	0.8
		Chelex Removeable	10.6	5.4	3.9	3.6
		Strongly Bound	6.0	10.1	5.1	1.6
	Suspended Solid $\mu\text{g g}^{-1}$	Exchangeable Carbonate and Hydrous Metal Oxide	1169.3	672.6	363.6	533.6
		Organic	407.7	196.0	39.4	120.5
			487.4	70.6	7.6	9.1
COPPER	Dissolved $\mu\text{g l}^{-1}$	Electrochemically Available	n.d.	n.d.	45.4	3.4
		Chelex Removeable	35.0	15.0	71.5	28.6
		Strongly Bound	12.8	3.5	66.7	5.6
	Suspended Solid $\mu\text{g g}^{-1}$	Exchangeable Carbonate and Hydrous Metal Oxide	66.2	31.6	610.2	649.6
		Organic	139.2	50.1	117.4	305.4
			221.4	35.6	29.0	28.9
PARAMETERS						
	Dissolved Organic C $\text{mg l}^{-1}$		7.0	-	8.9	5.5
	Dissolved Chloride $\text{mg l}^{-1}$		28.9	-	159.6	21.4
	Average pH Value		7.5	7.2	6.6	7.1
	Suspended Solids $\text{mg l}^{-1}$		102.8	113.7	122.6	69.6
	Suspended Solid Organic C $\text{mg l}^{-1}$		-	24.3	23.9	14.3
			n.d. = not detected			

Table 2. Loadings for the Heavy Metals and Parameters during each Storm Event.

	Storm Event			
	Oxhey 830224	Oxhey 830602	Bergsjön 831004	Bergsjön 831027
Flow, m <sup>3</sup>	2250	285	47	87
Dissolved Organic Carbon, kg	15.8	-	0.4	0.5
Dissolved Chloride, kg	64.9	-	0.8	1.9
Suspended Solids, kg	231.2	32.4	5.8	6.1
Zinc, g	519.8	51.2	11.1	18.0
Cadmium, g	21.9	1.1	0.2	0.2
Lead, g	516.3	34.9	3.9	4.5
Copper, g	206.4	12.1	10.9	9.3

### Partitioning of Metals between the Phases and Fractions

The percentage of each species in the storm events which have been studied are shown in Figure 2. Despite the occasional large differences of metal concentrations in each storm (Table 1) the proportioning of the metals between the fractions is remarkably comparable between storm events and catchments.

Zinc shows a presence in both the dissolved and suspended solid phases but is most important in the soluble form. In this phase the bioavailable Electrochemically Available and the Chelex Removeable fractions are 43% and 48% of the total metal respectively. For the suspended solid phase the bioavailable Exchangeable fraction is most important being 19% of the total metal. The dissolved Strongly Bound fraction is the more important removal and sink mechanism for zinc species accounting for 20% of the total metal, although the suspended solid Organic fraction (9%) is also significant.

In the case of cadmium almost all the metal is distributed in the bioavailable Electrochemically Available (52%), Chelex Removeable (57%) and Exchangeable (25%) fractions. Cadmium forms strong chloro complexes, which explains its solubility and ease of release from the solid phase. Therefore most of the cadmium transported by stormwater may have a direct impact on the receiving waters.

Lead is predominantly suspended solid associated with only 15% of the metal, on average, in the dissolved phase. Of the dissolved fractions the Strongly Bound fraction is usually the most important. This demonstrates that the presence of dissolved organic ligands in the aqueous system can increase the mobilisation and solubility of this element. In addition the suspended solid phase is largely dominated by the Exchangeable fraction (63%) which may be released into the water column where suitable conditions for solubilisation occur. The Carbonate and Hydrated Metal Oxide (14%) and Organic (8%) fractions are important transport mechanisms and sinks for lead.

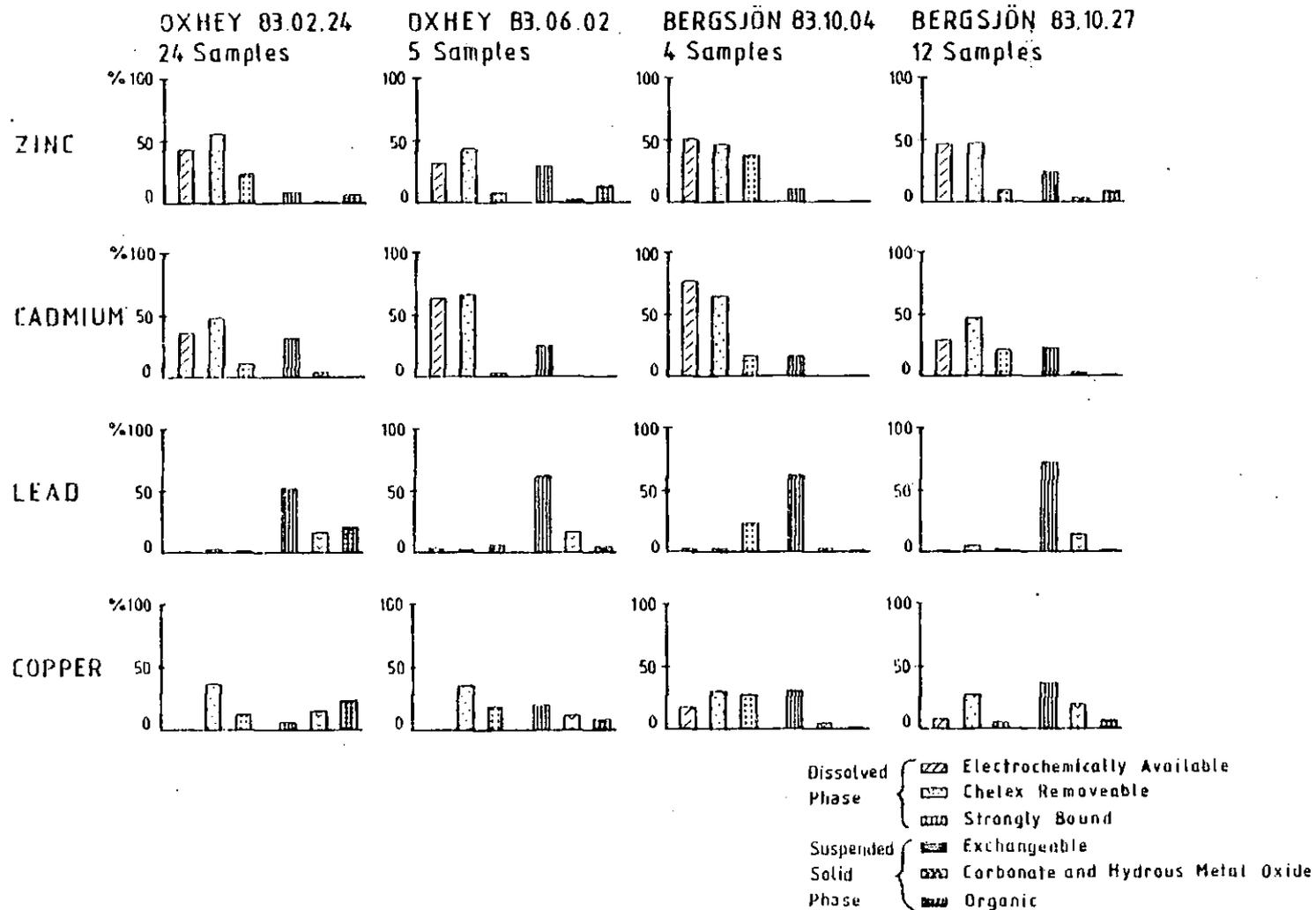


Figure 2. Distributions of Zinc, Cadmium, Lead and Copper between the Physico-Chemical Fractions for selected Storm Events (Dissolved Phase = Chelex Removeable + Strongly Bound).

Copper is found to be fairly evenly distributed between both the dissolved and suspended solid phases. Copper is readily complexed by dissolved organic compounds giving rise to only Chelex Removeable and Strongly Bound fractions in the UK catchment, but in the Swedish catchment the copper concentration is higher and so there is also the Electrochemically Available fraction present. A similar trend in the particulate phase shows a higher proportion of copper in the more readily released Exchangeable fraction in the Swedish compared to the UK catchment. However, for both catchments the combined Strongly Bound, Carbonate and Hydrous Metal Oxide and Organic fractions (42%) represent a significant sink for copper.

Metal speciation schemes which have been applied to the dissolved phase of freshwater (Duinker and Kramer 1977, Batley and Gardner 1978, Figura and McDuffie 1980, Pik et al. 1982) have shown that cadmium and zinc are mainly present as relatively free forms, which corresponds to our Electrochemically Available fraction. Soluble lead in freshwaters was found to exist mostly as inorganic complexes which corresponds in our scheme to metals released into the Chelex Removeable fraction but not the Electrochemically Available fraction. However, in stormwater the strongly bound lead also represents a significant contribution to the dissolved phase. In both freshwater and stormwater soluble copper is found to be predominantly associated with strongly bound complexes.

Most of the speciation work carried out on particulate associated metals has been concerned with river sediments (Gibbs 1973, Tessier et al. 1979, Salomons and Forstner 1980) and road sediments (Harrison et al. 1981, Hamilton et al. 1984). These studies have indicated that zinc and cadmium are mostly associated with the Hydrous Metal Oxide fraction, while copper and lead are distributed between the Hydrous Metal Oxide and Organic fractions. Cadmium showed the greatest tendency to be Exchangeable, but this fraction usually represented less than 10% of the total metal. Our results show important differences to these studies in that the Exchangeable fraction is found to be dominant for all the metals except possibly for copper in the UK catchment. These results agree with the trends observed by Forstner and Patchineelam (1980) which demonstrated an increase in the proportion of metals in the less stable fractions of sediments in more polluted waters. Particulate cadmium in all stormwater samples shows an almost negligible affinity for the Carbonate and Hydrous Oxide and Organic fractions. The unique association of cadmium with the Exchangeable fraction represents a potential toxic threat to the stormwater due to its experimentally determined solubility (Ellis and Revitt 1982).

#### ACKNOWLEDGEMENTS

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# THE TRANSPORT MECHANISMS, PHASE INTERACTIONS AND EFFECTS OF BIOAVAILABLE HEAVY METALS IN SNOWMELT RUNOFF.

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## SUMMARY

The identification, transport mechanisms and receiving water impacts of Zn, Cd, Pb and Cu species in urban snowmelt runoff are discussed. Temporal variations of bioavailable Zn and Cu are strongly dependent on suspended solid organic carbon discharges, while bioavailable Pb and Cd loadings are mainly controlled by dissolved chloride levels.

The metal speciation is explained in terms of two mechanisms; surface area adsorption and ionic strength.

All metals exceed EPA threshold toxicity levels whilst Cu and Cd are identified as causing significant mortality to freshwater life.

## INTRODUCTION

Urban runoff waters have been shown to contain high concentrations and loadings of heavy metals in the form of biologically and chemically reactive species (ref.1).

The actual bioavailable species appear to be the free metal ion and certain organic lipid soluble species (ref.2) and can be a considerable source of biotic toxicity in receiving waters (ref.3).

This paper investigates bioavailable heavy metal species in snowmelt runoff.

## CATCHMENT AND ANALYTICAL METHODS

Samples of snowmelt runoff were collected at the outfall of a 15.4 ha. urban residential catchment in Bergsjön, Goteborg, Sweden (ref.1).

The speciation scheme for the separation of heavy metal fractions has been fully described previously (ref.1, ref.4). The dissolved phase is separated into three fractions depending on the complexation strength of the heavy metals: Electrochemically Available (Bioavailable), Chelex Removeable (Bioavailable), Strongly Bound. The suspended solid phase is divided into three fractions according to the ease of metal release: Exchangeable, Carbonate and Hydrated Metal Oxide, Organic.

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## RESULTS AND DISCUSSION

The hydrograph for the snowmelt studied has an initial melting period of  $4\frac{1}{2}$  hours followed by a light rainfall event and a recessional limb during which snowmelt continued. The relatively low suspended solid concentrations of  $40 \text{ mg l}^{-1}$  during the early snowmelt rose to  $1600 \text{ mg l}^{-1}$  during the later rainfall runoff. Dissolved organic carbon, particulate organic carbon and dissolved chloride (up to  $17 \text{ g l}^{-1}$ ) show similar temporal peak variations during the snowmelt. The pH at the outfall varies between 6.7 and 7.4 despite a value of 4.0 in the rainfall itself.

Bioavailable Cd and Pb have similar hydrographic loading variations to the controlling parameters. Pb has a peak dissolved bioavailable concentration of  $330 \text{ } \mu\text{g l}^{-1}$  due to the solids being stripped of Pb by associated high chloride levels. Cd shows an even greater tendency to be solubilised by chloride.

The bioavailable Zn and Cu are present in their lowest concentrations during the majority of the snowmelt due to the high particulate concentrations. However, dissolved bioavailable concentrations reach  $558 \text{ } \mu\text{g l}^{-1}$  and  $146 \text{ } \mu\text{g l}^{-1}$  for Zn and Cu respectively, when suspended solid levels decrease on the receding limb of the hydrograph.

Consideration of overall metal speciation demonstrates (Figure 1), that for all four metals the early snowmelt and recessional limb show similar proportions of metal species to those found in stormwater samples (ref.1). However, the higher chloride concentrations of the snowmelt result in an increase in the proportion of soluble Cd and Pb species, especially during the rainfall event when chloride concentrations are at their highest.

In contrast, Zn and Cu exhibit a strong affinity for the Organic fraction of the suspended solid phase, especially during the rainfall stage when high suspended solid concentrations are found.

The results for previous stormwater data (Morrison et al 1984) and the snowmelt event described in this paper, can be consolidated to provide two possible mechanisms for metal uptake onto, and release from, suspended solids.

### 1. Metal adsorption onto the particulate surface.

Previous workers (ref.5) have demonstrated that at low suspended solid concentrations, which are usually associated with low flow conditions, small particles containing elevated metal levels are preferentially washed off the urban surface. However, a surface area uptake theory adequately explains the relationship between particle size and metal concentration. A plot of particle diameter ( $\mu\text{m}$ ) versus surface area per unit weight ( $\text{cm}^2\text{g}^{-1}$ ), assuming a particle cut-off size of  $0.4 \mu\text{m}$  and a particle density of between 1.0 and  $2.7 \text{ g cm}^{-3}$ , gives a hyperbolic relationship. A similar relationship between suspended solid concentrations and the levels of particulate associated metals has been found for urban catchments in both Sweden and the U.K.

The proposed mechanism for metal transport is that during rainfall, which usually has a pH of 3.5 to 5.0 at

SNOWMELT, BERGSJÖN 20.12.83

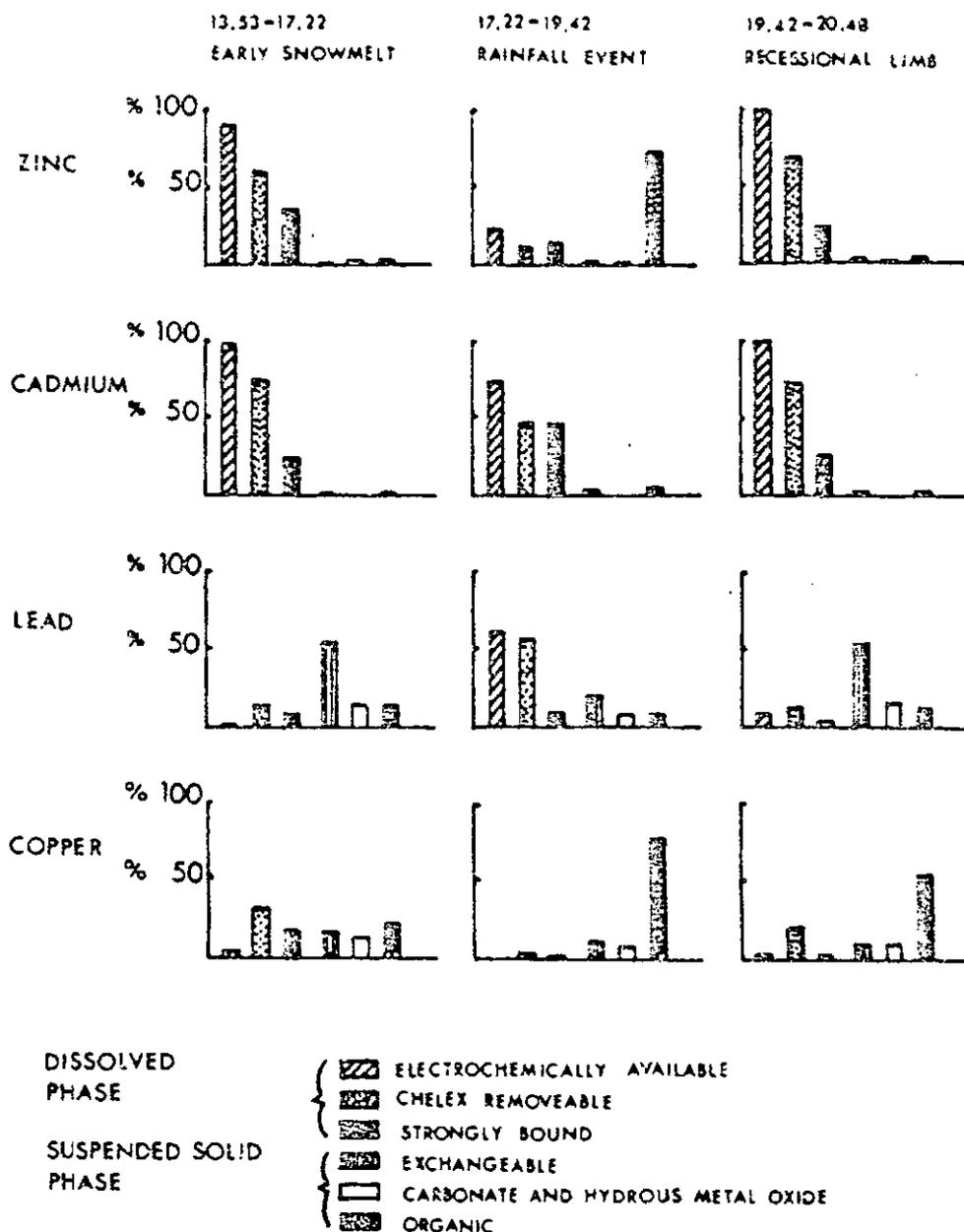


Figure 1:- Distribution of Metal Fractions through the Snowmelt Event.

Bergsjön, some heavy metals are washed off the urban surface and solubilised. At a point between the urban surface and the storm sewer outfall the pH is buffered up to between 6.5 and 8.0, and the dissolved metals become adsorbed onto the surface of the suspended solids.

2. Ionic Strength

The first process is counteracted in snowmelt by the independent action of ionic strength. High ionic strength occurs in stormwater runoff when urban surfaces are heavily salted during periods of snowfall. The high chloride concentrations assist desorption of heavy metals from suspended solids into

the dissolved phase, especially for metals such as Cd and Pb which form strong chloro complexes.

The toxic impact of snowmelt heavy metals towards freshwater life is considered using EPA standards for intermittent discharges. Zn, Cu and Cd exist in the outfall waters for considerable periods above the threshold limit, while Cu and Cd exceed the level of significant mortality for 4.1 and 0.8 hours, respectively. The high levels of Cu are due to the preponderance of copper guttering at Bergsjön, but for Cd more research is required to determine the origins, effects and recurrence intervals of Cd discharged from urban catchments.

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THE TRANSPORT MECHANISMS AND PHASE INTERACTIONS OF BIOAVAILABLE HEAVY METALS IN SNOWMELT RUNOFF

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Abstract

The identification and transport mechanisms of Zn, Cd, Pb and Cu species in urban snowmelt runoff are investigated.

Bioavailable metal species in snowmelt occur in higher concentrations than in stormwater from the same catchment. Temporal variations of Zn and Cu are strongly dependent on suspended solid organic carbon discharges, while Pb and Cd loadings are mainly controlled by dissolved chloride levels.

The metal speciation variations throughout the snowmelt process are explained in terms of two mechanisms; surface area adsorption and ionic strength.

When the toxic impacts and effects of bioavailable heavy metal species on

the receiving water biota are evaluated according to proposed EPA standards for intermittent discharges then all metals exceed the threshold toxicity levels, whilst Cu and Cd are identified as being able to cause significant mortality to freshwater life.

## Introduction

Urban runoff waters have been shown to contain high concentrations and loadings of heavy metals in the form of biologically and chemically reactive species (Morrison and others 1984a). Zn, Cd and Cu have been found to be predominantly associated with the dissolved phase, whilst Pb has a strong affinity for the suspended solid fraction. Metal distributions are also dependent on parameters such as suspended solid concentrations and ionic strength (Morrison and others 1984b). The actual bioavailable metal species in the aqueous environment appear to be the free metal ion and certain organic lipid soluble metal species (Florence and others 1983).

Snow has been shown to accumulate heavy metals (Vuorinen 1983) and their subsequent release as potentially toxic forms may occur during melting. In order to assess the potential toxicity of these pollutants during this process, the determination of the metal speciation is described in this paper. In addition, the heavy metal exchange mechanisms between the solid and liquid phases and their importance in the transfer of metals from urban snowmelt runoff into receiving waters are discussed.

## Catchment and Analytical Methods.

Samples were collected at the outfall of a 15.4 ha. urban residential catchment in Bergsjön, Göteborg, Sweden. The hydrology and instrumentation

of the catchment have been fully described by Arnell (1980) and Malmqvist (1983).

The speciation scheme (Fig. 1) for the separation and identification of heavy metal fractions in stormwaters has been fully described elsewhere (Morrison 1983, Morrison and others 1984a). The dissolved phase is separated into three fractions which are dependent on the complexation strengths of the heavy metals; the Electrochemically Available and Chelex Removeable fractions are considered to be bioavailable. For the purpose of distinguishing bioavailable metals the fraction with the greater concentration of metal ion is reported here. The suspended solid phase is divided into three fractions according to the ease of metal release to the soluble phase. Of these, only the Exchangeable fraction is regarded as potentially bioavailable.

## Results and Discussion

### Snowmelt Runoff

The hydrograph and chemographs for selected parameters are shown in Fig. 2(a) to (d). An early snowmelt period of 4½ hours was followed by a light rainfall event of 0.2 mm hr<sup>-1</sup> intensity which greatly increased the flow. Snowmelt continued during the recession limb on the hydrograph. The relatively low suspended solid concentrations of approximately 40 mg l<sup>-1</sup> observed during the early snowmelt rose to 1600 mg l<sup>-1</sup> during the later rainfall with particulate organic carbon following similar temporal trends. Dissolved organic carbon also followed the same, although less pronounced pattern. An inspection of Fig. 2(a) and (b) shows that the mass flow of particulate organic carbon may be up to 40 times higher than dissolved

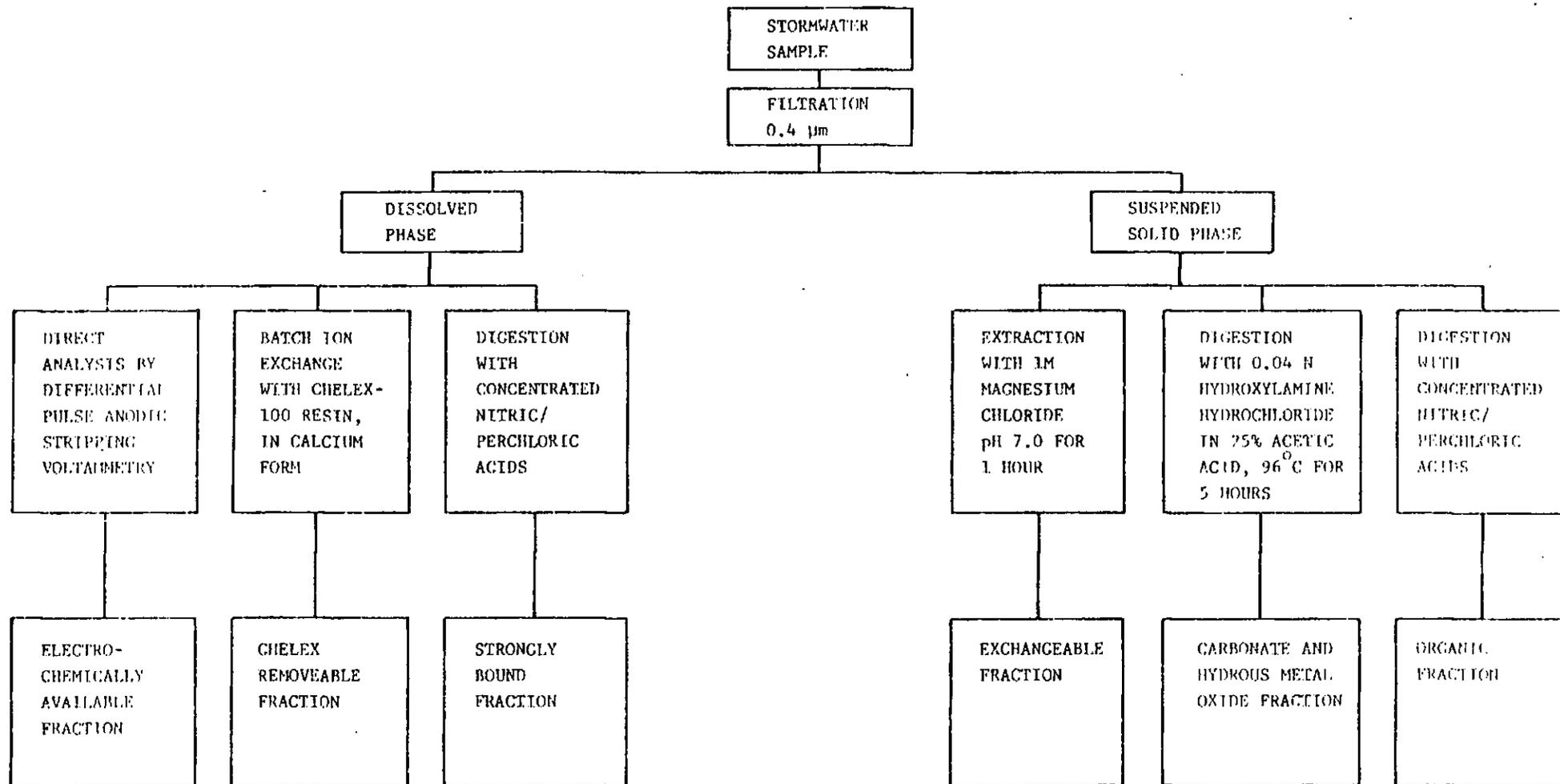


Fig. 1 The Scheme of Analysis for Heavy Metal Speciation.

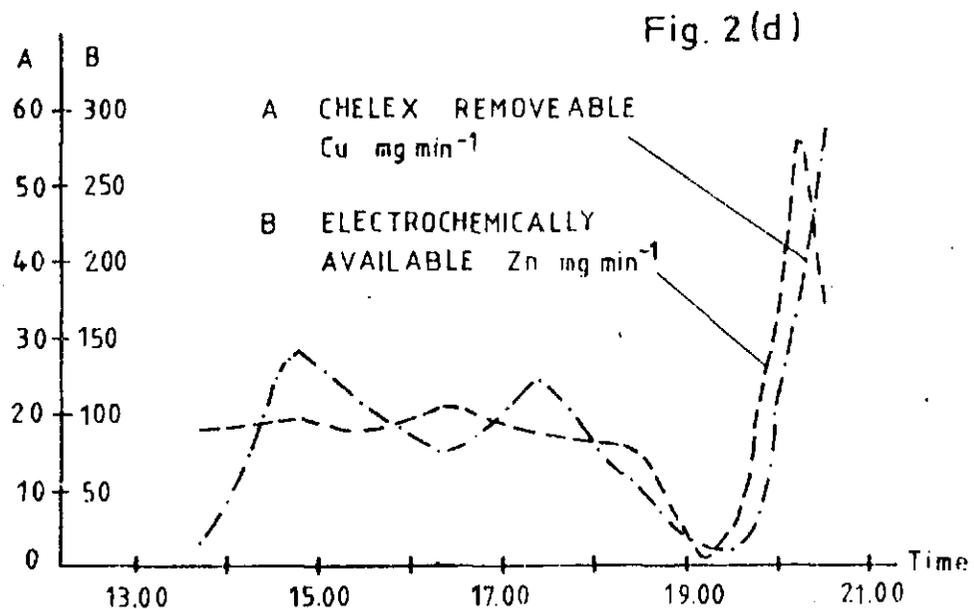
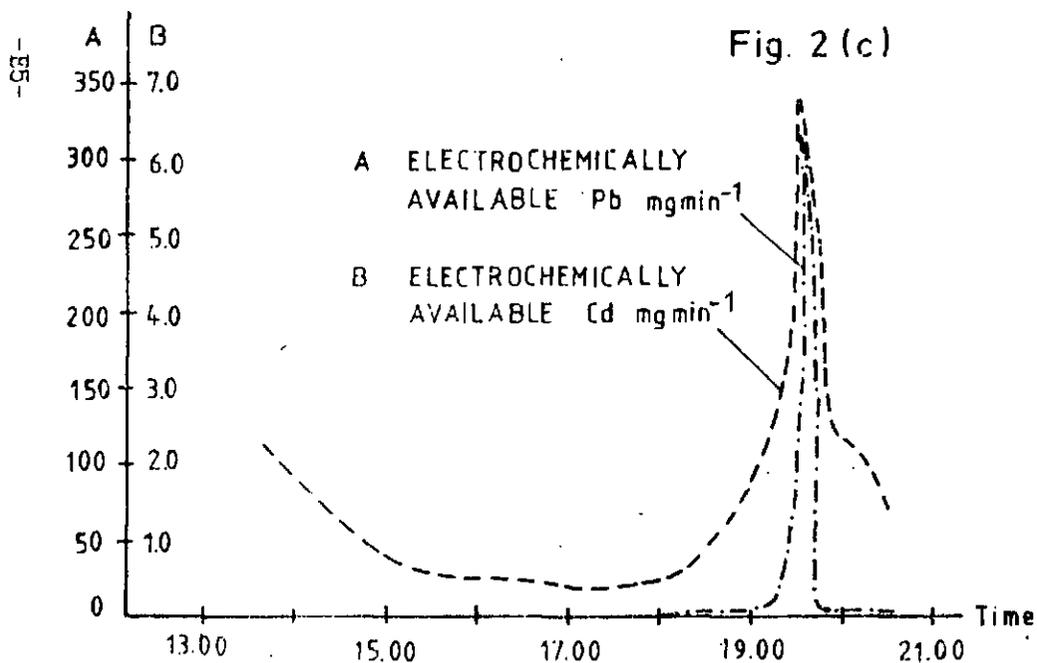
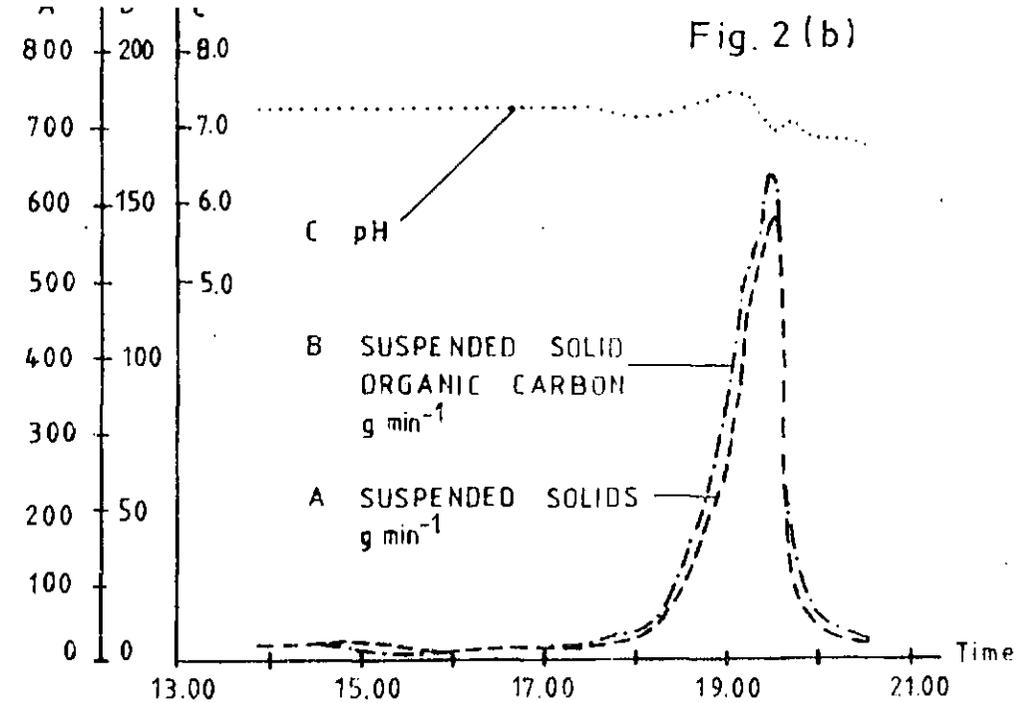
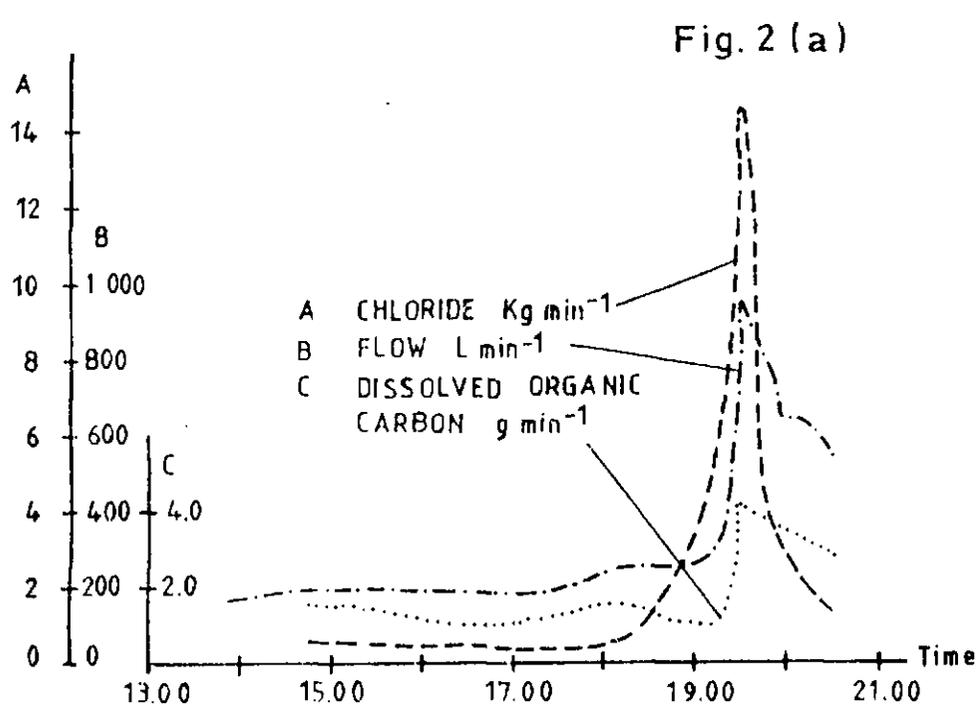


Fig. 2 Hydrograph and Chemographs for the Snowmelt Runoff Event 20.12.83.

organic carbon. Assuming that similar metal complexation stability constants exist for the dissolved and particulate organic carbon compounds, then particulate organic carbon is more important for the solid/aqueous phase partitioning of the metals. Dissolved chloride levels (Fig. 2(a)) are fairly high throughout the hydrograph but reach elevated concentrations, similar to those in sea water, during the rainfall event. It is probable, therefore, that chloride will cause significant metal solubilisation particularly during the washoff processes associated with the onset of the rainfall event. The pH values at the outfall (Fig. 2(b)) show only a small variation between 6.7 and 7.4. This neutral pH occurs despite an incoming rainfall pH of 4.0 and is apparently due to stormwater buffering which occurs between the road surface and the end of pipe.

The chemographs for the Electrochemically Available fractions of the dissolved metals show that bioavailable Cd and Pb (Fig. 2(c)) have similar loading variations to the controlling parameters described above and in particular dissolved chloride, except that Cd has a fairly high value early in the snowmelt period. The Pb distribution can be explained by its affinity for the particulate phase (Morrison and others 1984b). During the early stages of snowmelt, the slow continuous release of solids results in high concentrations (up to  $1075 \mu\text{g g}^{-1}$ ) of particulate associated Pb. It is probable that much of this Pb originates from vehicular emissions which become attached to particulates lying on the road surface. At the onset of rainfall a high suspended solids concentration occurs but the resulting solids are stripped of Pb by the associated high chloride levels. The result is a rapid rise in the loading of bioavailable dissolved Pb which attains a peak concentration of  $330 \mu\text{g l}^{-1}$ .

Cd shows high dissolved bioavailable concentrations at the onset of both snowmelt and rainfall, with concentrations of up to  $12.5 \mu\text{g l}^{-1}$ . This demonstrates both the ease with which washoff of soluble Cd occurs (Ellis and Revitt 1982) and its similarity to Pb in the ability to form strong chloro-complexes.

The loadings of Electrochemically Available Zn and Chelex Removeable Cu (Fig. 2(d)) show early small peaks and a delayed response for the main peak compared to other parameters. Thus Zn and Cu are present in their lowest bioavailable concentrations at the onset of the rainfall event. The high suspended solid and particulate organic carbon concentrations probably control the partitioning of these metals at this stage and the soluble levels increase only as these decrease. Zn and Cu originate predominantly from roof and surface corrosion and have peak dissolved bioavailable concentrations of  $558 \mu\text{g l}^{-1}$  and  $146 \mu\text{g l}^{-1}$  respectively.

#### Metal Speciation through the Snowmelt Event

The metal speciation distributions in the three distinct parts of the snowmelt event are identified in Fig. 3 together with previous stormwater results observed for Bergsjön. For all four metals, the early snowmelt and recession limb stages show similar proportions of metal species to the averaged stormwater events. However, there is a tendency for less total metal to be found in the stormwater dissolved phase probably because of the presence of lower dissolved chloride concentrations compared to the snowmelt. The overall dissolved organic carbon concentrations and pH values are similar in both snowmelt and stormwater.

SNOWMELT EVENT 20.12.83

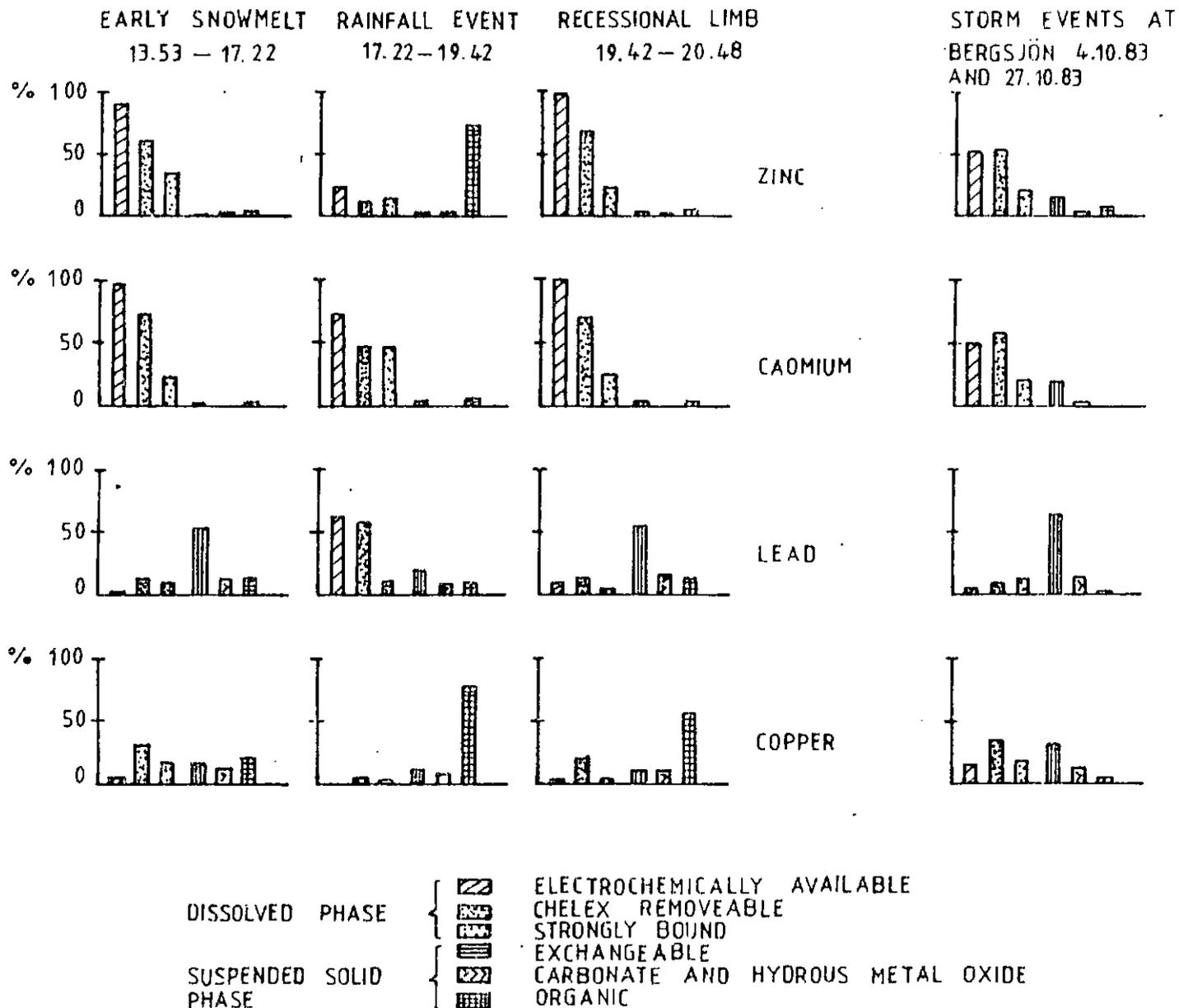


Fig. 3 Comparison between the Heavy Metal Speciation in the Snowmelt Event and Stormwater.

At the commencement of the rainfall event the dissolved chloride concentrations increase and result in a stripping off of about 50 percent of the Exchangeable Pb. The Pb then takes the form of Electrochemically Available and Chelex Removeable species, with no significant addition to the Strongly Bound fraction. On the recessional limb the Pb distribution pattern again becomes comparable with that during early snowmelt.

Even at the low chloride concentrations of stormwater which occur in autumn, Cd is still very soluble and therefore of considerable potential toxicity. The relatively high chloride concentrations during all stages of snowmelt mean that the Exchangeable fraction of Cd in the suspended solids is unimportant.

The decrease of dissolved bioavailable Zn and Cu loadings in the rainfall event, and for Cu on the subsequent hydrograph recessional limb, can be explained by uptake into the Organic fraction of the suspended solid phase (Fig. 3). The distribution of the metals between the fractions confirms that for Zn and Cu the particulate organic carbon is an important control during snowmelt conditions when suspended solids loadings are high.

The Electrochemically Available fraction is occasionally higher than the Chelex Removeable fraction, particularly for Zn and Cd in snowmelt samples. The electrochemical technique may therefore, in these instances, be detecting some metals which are relatively strongly bound and yet inert to Chelex-100. Florence (1982) and Batley (1983) have accounted for these kinetic problems by suggesting that the lability concept of Figura and McDuffie (1980) is not always applicable in natural water systems. It could also be the case in stormwater that dissolved organic carbon, in greater

concentrations than river or sea water, may readily attach to the surface of the chelating resin and so prevent the metal ion exchange process.

### Dissolved and Suspended Solid Phase Interaction Mechanisms

The results for previous stormwater data (Morrison and others 1984a) and the snowmelt event described in this paper, have been consolidated to provide two possible mechanisms for metal uptake onto, and release from, suspended solids.

#### 1. Metal adsorption onto the particulate surface.

Harrison and Wilson (1983) have demonstrated that at low suspended solid concentrations, which are usually associated with low flow conditions, small particles containing elevated metal levels are preferentially washed off the urban surface. During higher flows which also contain larger particles, rather lower suspended solid metal concentrations are found and it has been proposed that the hydrodynamic sorting of highway surface dust might explain these results. However, metal concentrations in stormwater solids are generally much higher than even the fine fractions of road dusts (Morrison and others 1984 b). A surface area uptake theory adequately explains the relationship between particle size and metal concentration. A plot of spherical particle diameter ( $\mu\text{m}$ ) versus surface area per unit weight ( $\text{cm}^2 \text{g}^{-1}$ ) gives a hyperbolic relationship.

A similar relationship between suspended solid concentrations and the concentrations of particulate associated metals (Table 1) has been found for urban catchments in Sweden and the U.K. If it is accepted that small particles are prevalent during low flow conditions then the results show that surface area related uptake is an important mechanism for particulate

Table 1. The Relationship between Suspended Solid Concentration  $\text{mg l}^{-1}$  (X-axis) and Suspended Solid Associated Metal Levels  $\mu\text{g g}^{-1}$  (Y-axis).

		Equation $YX = K$	Linear Regression for logged equation $r$	t-Test significance %
Zn	Stormwater, Bergsjön, Sweden*	$YX^{0.74} = 15,690$	0.52	95
	Snowmelt, Bergsjön, Sweden	$YX^{0.26} = 1,827$	0.32	80
Cd	Stormwater, Oxhey, U.K.*	$YX^{1.44} = 11,473$	0.79	99
	Snowmelt, Bergsjön, Sweden	$YX^{0.48} = 20$	0.43	80
Pb	Stormwater, Bergsjön, Sweden*	$YX^{0.31} = 2,049$	0.23	80
	Snowmelt, Bergsjön, Sweden	$YX^{0.53} = 5,045$	0.89	90
Cu	Stormwater, Bergsjön, Sweden*	$YX^{0.5} = 7,188$	0.33	90
	Snowmelt, Bergsjön, Sweden	$YX^{0.89} = 117,809$	0.95	90

\* Data from Morrison and others (1984a)

metal transport. The relationship could be usefully applied to the modelling of stormwater and snowmelt metal discharges from urban areas.

The proposed mechanism for metal transport would envisage that during rainfall, which usually has a pH of 3.5 to 5.0 at Bergsjön, some heavy metals are washed off the urban surface and solubilised. Somewhere between the urban surface and the storm sewer outfall the pH is buffered up to between 6.5 and 8.0, and the dissolved metals become adsorbed onto the surface of the suspended solids.

The evidence from Fig.3 suggests that particulate organic carbon may play a significant role in this mechanism, adsorbing metals onto the surface when a sufficient increase in pH has occurred. The extent of this uptake depends on the surface area of the particles. A certain amount of each metal remains in the dissolved phase and in stormwater significant correlations have been found with dissolved organic carbon (G.M.P. Morrison, unpub. data). However, in snowmelt ionic strength is also regulating metal partitioning between the dissolved and suspended solid phases.

## 2. Ionic Strength.

The above process is counteracted in snowmelt by the independent action of ionic strength. High ionic strength occurs in stormwater runoff when urban surfaces are heavily salted during periods of snowfall. A comparison of Fig. 2(a) and (b) shows that considerably greater loadings of dissolved chloride were discharged during the monitored snowmelt event than for either dissolved or particulate organic carbon. The high chloride concentrations assist desorption of heavy metals from the suspended solids into

the dissolved phase, especially for metals which form strong chloro complexes such as Cd and Pb. Relatively high levels of chloride, such as those found in snowmelt runoff, must be present for this process to be important. The results of this work suggest that the influence of high chloride levels is the most important factor controlling Pb and Cd distributions between the solid and aqueous phases. For Cu and Zn particulate organic carbon appears to be the most important controlling parameter, especially when high suspended solid loadings are present.

### The Toxic Impact of Heavy Metals in Snowmelt Runoff to Freshwater Life

Both EPA (EPA 1984) and EEC (Mance and O'Donnell 1984) standards have been considered with regard to potential toxic impacts on freshwater life in receiving waters. Only the proposed EPA recommended standards take account of intermittent discharges and these are listed in Table 2 together with the time period that these levels were reached and exceeded in the snowmelt event. It is important to point out that these must be considered to be minimum effects as the EPA threshold values are for total metal concentrations which are compared to the bioavailable dissolved metal values determined in this study. It is also recognised that there will be further dilution of metal concentrations on entering the receiving stream.

Table 2 shows that Zn, Cu and Cd in the outfall waters exist for considerable periods above the threshold limit, while Cu and Cd exceed the level of significant mortality for 59 and 12 percent of the snowmelt respectively. Cu exceeds this level during both early snowmelt and throughout the recession limb of the hydrograph. The presence of high suspended solid loadings during the rainfall stage of the event (Fig. 2) rapidly lowers the soluble concentration to a value below the toxicity threshold. Cd exceeds

Table 2. EPA Recommendations for Intermittent Exposure and the Percentage Time for which these Values were exceeded in Snowmelt Runoff.

	EPA Threshold Toxicity		EPA Significant Mortality	
	Metal Concentration $\mu\text{g l}^{-1}$ *	Time exceeded %	Metal Concentration $\mu\text{g l}^{-1}$ *	Time exceeded %
Zn	380	61	870-3200	-
Cd	3	42	7-160	12
Pb	150	3.6	350-3200	-
Cu	20	77	50-90	59

\* Data from EPA (1984)

the significant mortality level during the first stages of early snowmelt and the rainfall event but decreases as the chloride loadings are depleted.

These results can be compared with a previous study of the Bergsjön urban catchment (Malmqvist 1983) in which average total heavy metal concentrations were determined for 19 storm events over a year. For Zn, Pb and Cu, 53%, 63% and 100% respectively of the storm events contained average total metal concentrations above the toxicity threshold value in Table 2. This suggests a significant intermittent impact on receiving waters which is underlined by the 11% (Zn), 16% (Pb) and 95% (Cu) of the storms which were also above the significant mortality level.

#### Acknowledgements

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SECTION 1. ANALYTICAL, C. ENVIRONMENTAL ANALYSIS

A PHYSICO-CHEMICAL SPECIATION SCHEME FOR THE ANALYSIS OF CADMIUM, COPPER, LEAD AND ZINC IN URBAN STORMWATER RUNOFF

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A speciation scheme has been devised which provides a relatively rapid technique for separating the dissolved and suspended solid phases of stormwater into fractions which possess differing degrees of metal bioavailability. The soluble phase is defined as that which passes through a 0.4  $\mu\text{m}$  Nucleopore polycarbonate filter and is subsequently separated into 3 fractions. The Electrochemically Available Fraction, which can be directly compared to the bio-available metal, is determined by Differential Pulse Anodic Stripping Voltammetry (DPASV). A batch extraction with Chelex-100 (Chelex Removable Fraction) enables those metals which are more strongly complexed to be estimated and the Strongly Bound Fraction is assessed following metal solubilisation by digestion with an oxidising mixture of concentrated nitric and perchloric acids (9:1 v/v).

The suspended solid phase is divided into 3 fractions, which are indicative of the ease of metal release to the soluble phase, by a series of sequential extractions. The Exchangeable Fraction, obtained by treating with 1M  $\text{MgCl}_2$  represents those particulate associated metals which may readily transfer to the dissolved phase under normal pH conditions. The more strongly bound metals in the combined Carbonate and Hydrrous Metal Oxide Fraction are determined by leaching with a solution of 0.04M hydroxylamine hydrochloride in 25% acetic acid and the remaining organically bound metals (Organic Fraction) are estimated by DPASV analysis after concentrated acid digestion. Application of this speciation scheme to urban stormwater samples indicates that potentially toxic forms of the metals in the dissolved phase (Electrochemically Available) and in the particulate phase (Exchangeable) can account for 63% of the total Zn, 77% of the total Cd, 66% of the total Pb and 32% of the total Cu.



## THE CONTINUOUS ON-LINE MONITORING OF ENVIRONMENTAL POLLUTANTS IN STORMWATER

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### Abstract

A monitoring system is described which provides continuous measurements of selected pollutants in stormwater.

The system, which has been installed at both the outfall to a stormwater pipe system and in a gullypot, is sensitive to changes in pH, conductivity, dissolved oxygen concentration, temperature and redox potential.

At the stormwater outfall monitoring station rapid changes of conductivity and turbidity are associated with the incoming rainfall, while the pH change is less sensitive due to road surface and in-pipe buffering. Temperature changes provide an indication of in-pipe water reservoir flushing.

The gullypot exhibits a significant drop in redox potential and dissolved oxygen concentration with incoming road runoff due to the mobilization of oxygen demanding, reduced bottom sediments and associated interstitial waters. During storm events the road surface material and the gullypot contents act as buffering media. Significant buffering of the gullypot water occurs between storm events due to the dissolution of the gullypot cement structure.

### Sammanfattning

Ett mätsystem beskrivs för kontinuerlig observation av utvalda dagvattenföroreningar. Mät-systemet, som har installerats i en mätstation för dagvattenavrinning och i en rännstensbrunn, kan registrera förändringar i flöde, pH-värde, konduktivitet, syrekoncentration, temperatur och redoxpotential.

I dagvattenavrinningen har stora förändringar i konduktivitet och turbiditet observerats, vilka samvarierar med regnintensiteten. Genom buffertverkan från vägytor och ledningar förändras pH-värdet i mindre grad. Temperaturförändringar kan visa på utflöde av vatten som magasineras i ledningar och rännstensbrunnar.

Vattnet i rännstensbrunnen visar en betydande sänkning i redoxpotential och koncentration av löst syre när de syrekrävande, reducerade bottensedimenten sätts i rörelse av inkommande vatten. Medan avrinningen pågår buffras dagvattnet av ytmaterialet på gatan och innehåller i rännstensbrunnen. Under torrperioder buffras vattnet i rännstensbrunnen genom utlösning av cement från väggarna i brunnen.

### Introduction

The continuous monitoring of environmental pollutants eliminates many of the problems associated with discrete sample collection and off-line analysis.

In this paper we discuss the design of and present some results for a continuous flow system which has been used to determine fluxes of contaminants in stormwater and through a roadside gullypot.

### Continuous on-line monitoring system

The system has been installed at the outfall to an urban stormwater pipe network in Bergsjön, Göteborg and adjacent to a roadside gullypot at Chalmers University of Technology, Göteborg.

### Continuous measurements at a stormwater sampling station

Bergsjön is a 15.4 hectare residential catchment in the northeast suburb of Göteborg. The outfall

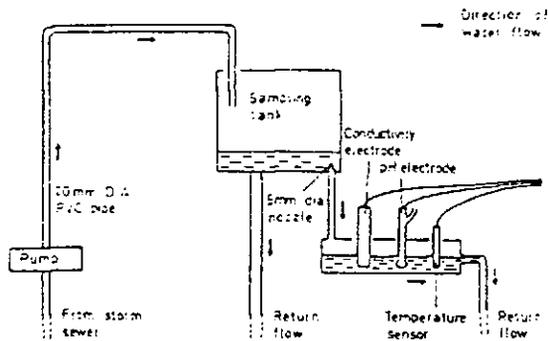


Figure 1. The continuous monitoring system inside the Bergsjön field station.

from the catchment drains into a small stream which enters the Sävve river. The continuous monitoring system has been installed inside the sampling station at the outfall (Figure 1).

Before sampling, the turbidity is recorded in the stormwater pipe to give an indication of suspended solid concentrations. Water level is measured over a calibrated V-notch weir by an ultrasonic sensor.

Water is continuously withdrawn from the baseflow, through a 20 mm PVC pipe, by a Johnson F5B-1 Impellor pump at a rate of 34 litres  $\text{min}^{-1}$ . After passing through a sampling header tank the water flows into the continuous monitoring system passing initially through a 5 mm nozzle and into a 12 mm diameter PVC tube at a rate of 0.7 litres  $\text{min}^{-1}$ . This final flow rate is stable during storm events.

The continuous flow system is constructed from a sealed PVC pipe of 70 mm diameter and 500 mm length. A 14 mm diameter hole on top of the pipe allows entry of the water, while the outlet is a 16 mm hole at the end of the system. This results in a flow depth during normal operation of 38 mm. Further holes allow the insertion of a series of sensors, which include a conductivity electrode, a temperature sensor and a pH electrode.

The electrode signals, which are amplified to between 0 and 10 mV, are recorded on a Chino 12 channel chart recorder. Facilities have now also been installed to digitally record the data utilising an ABC80 microcomputer. A program has been specially written for the system called "CTHVA1". The system also includes possibilities for computer controlled bottle sampling.

Calibration of the electrodes is carried out at least once a week, but apart from this the system requires very little maintenance. However, during storm events a high level of suspended solids may create blockages in the system. This has been

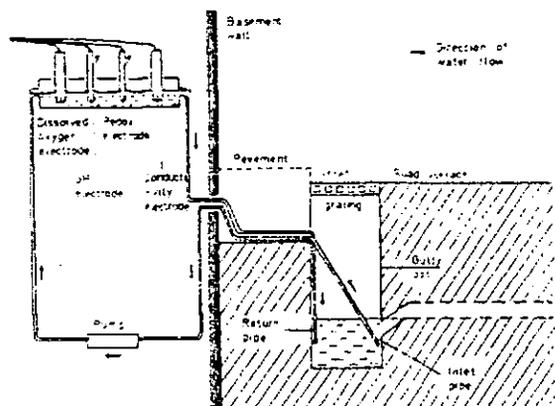


Figure 2. The continuous system for monitoring the contents of a gullypot.

prevented by attaching a 5 mm plastic mesh around the inlet pipe to the sampling tank and also around the continuous system inlet nozzle. The temperature sensor provides a useful indicator of system blockage as the readings equilibrate with the external temperature of the field station when the flow has stopped.

#### Monitoring a roadside gullypot

This system has been designed to continually sample gullypot water content and to provide a record of pH, dissolved oxygen, conductivity and redox changes with time (Figure 2).

Water is pumped out of the gullypot, through an opening in the basement wall, via a strength-

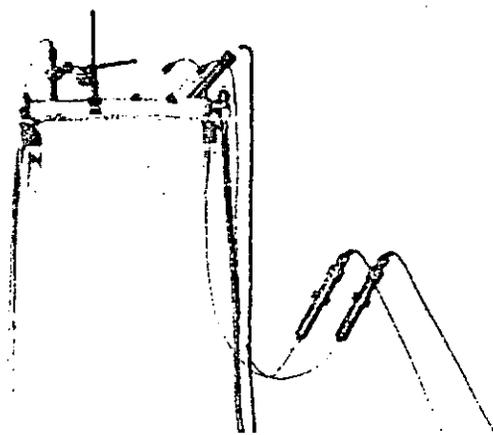


Figure 3. The continuous on-line monitoring system for the gullypot.

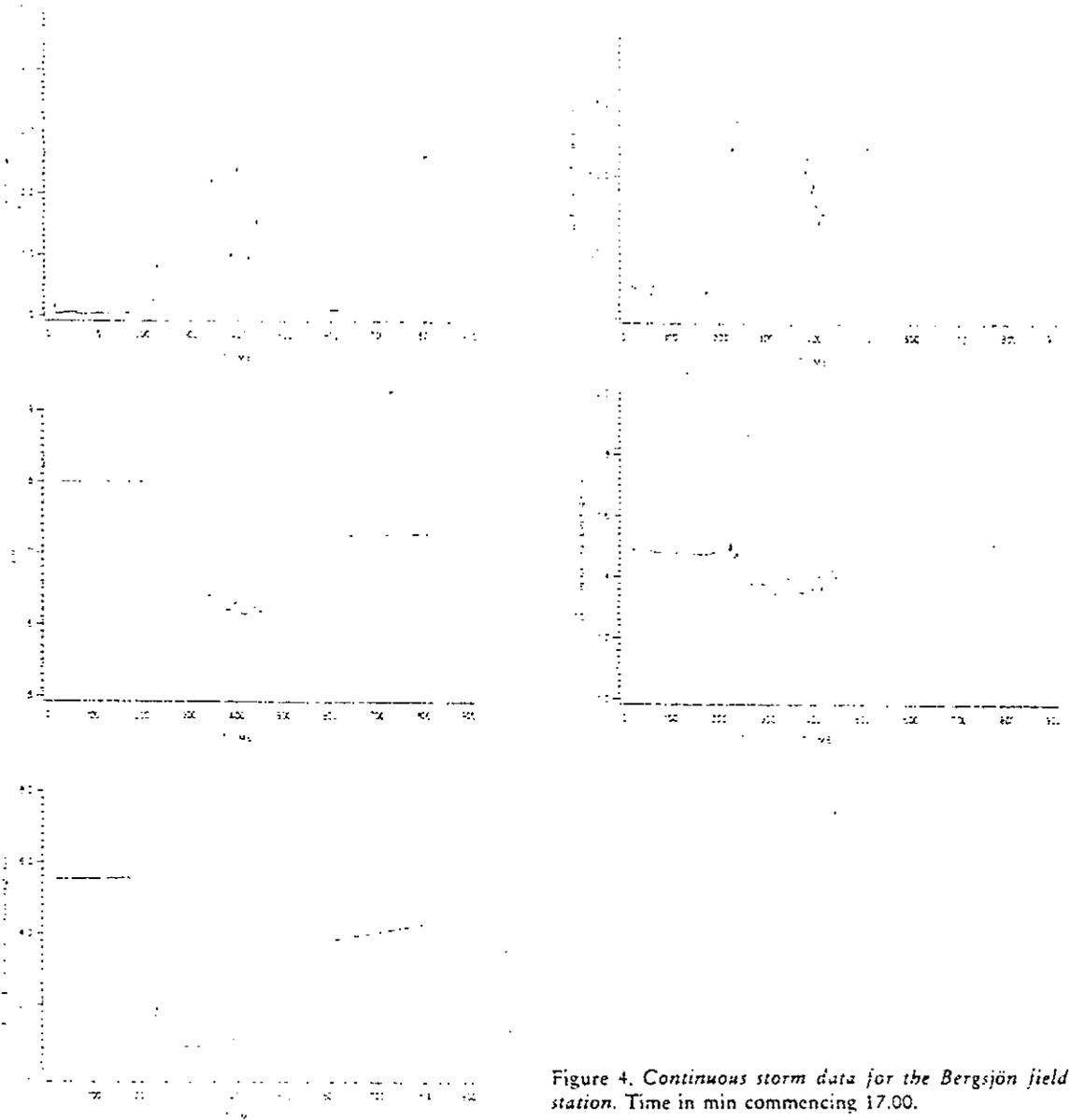


Figure 4. Continuous storm data for the Bergsjön field station. Time in min commencing 17.00.

ened 12 mm diameter plastic pipe and returned to the gulypot in the same manner after passing through a small Jabasco cog wheel pump and the on-line measurement system. A water flow rate of 2.6 litres  $\text{min}^{-1}$  allows a water depth of 30 mm to be maintained in the continuous system which is high enough to prevent blockage by solids. In this way the gulypot contents are recycled every 0.3 hours during dry conditions. Cleaning of the pipes is achieved by reversing

the pump and flushing with 2—3 litres of distilled water. This procedure is normally repeated twice a week or more frequently during periods of heavy rainfall.

The continuous monitoring system is a sealed PVC pipe of 50 mm diameter and 400 mm length, with an inlet of 13 mm diameter and an outlet of 25 mm diameter at the opposite end. Dissolved oxygen, combined redox potential, combined pH and conductivity electrodes are positioned, cali-

brated and the signals recorded in the same way as at Bergsjön.

A gullypot road runoff sampler, constructed at the University of Lund, is installed in the gullypot. Flow into the sampler is measured through a 30° V-notch weir and detected by a conductivity cell.

### Results of continuous storm data from the stormwater sampling station

A typical storm profile from the Bergsjön stormwater sewer system is shown in Figure 4.

An increase in the incoming flow is followed immediately by changes in conductivity. This indicates dilution of the baseflow, which usually contains 100–200 mg Cl l<sup>-1</sup>, by the incoming rainfall and runoff. On the recession limb of the storm event the higher baseflow conductivity is re-established.

The change in pH is slower and does not represent the rainfall pH, which is typically ca. 4.0. During storm events buffering can be attributed to the washing of road surfaces and the flushing of gullypots on the catchment. In addition it is thought that dissolution of the cement in the concrete pipe network is an important source of bicarbonate ions. The contact time of rainfall with the rather large surface area of the storm sewer pipes may be up to a few minutes between the catchment and end-of-pipe.

Changes in turbidity have been gravimetrically calibrated with samples of stormwater solids and provide an important indication of suspended solid transport rates. As is evident from Figure 4 variations of turbidity are characterised by a "first flush" followed by a less important "secondary flush". For 190 storm events, monitored in this way during 1983 and 1984, 54 % were characterized by a "first flush" in terms of turbidity. It can be argued that the "first flush" is a combination of road surface, gullypot and in-pipe sediment washoff. The energy for road surface sediment washoff is created by the process of surface wetting, rainfall intensity and hydraulic surface flow. Gullypot and in-pipe sediment mobilization are dependent on the water flow energy and the nature of the sediments.

Temperature changes generally follow conductivity and pH, with a decrease in temperature associated with incoming rainfall. However, the slight increase in temperature at the very beginning is characteristic of most storm events in autumn. Gullypots are the only reservoir of relatively warm water, compared to baseflow, and their flushing at the commencement of the storm

event seems the most likely explanation for this initial temperature increase.

### Interpreting storm data from the roadside gullypot

The continuous data obtained from the gullypot shows rapid changes and is less complicated than the response at the end of the stormwater pipe network (Figure 5). The gullypot has a standing volume of 41.5 litres.

Two distinct types of storm event have been observed in the gullypot, as seen in Figure 5a and Figure 5b.

A small rainfall event of 128 litres runoff is shown in Figure 5a, which is only sufficient to mix, but not completely flush, the gullypot. A lag period of 5 min is observed between the commencement of flow and any observed change in either dissolved oxygen or redox potential. The significant drop which eventually occurs in redox potential and dissolved oxygen concentration represents a mixing of the reducing, oxygen demanding interstitial water and bottom sediments. At the same time a mobilisation of sediment associated salts and organics occurs which cause a general increase in conductivity at the end of the storm event.

The reading for pH generally increases between storm events from ca. 4.5 up to 7.0, because of dissolution of the gullypot cement structure. However, despite a measured incoming rainfall pH of 4.0 and complete sediment mixing after 5 min, pH changes within the gullypot lag 14 min behind the commencement of flow. This represents the residual buffering capacity of the gullypot. The resultant titration curve is a slight overestimate of the gullypot buffering capacity as the road surface and its associated sediments also buffer the acidic rainfall.

A second type of rainfall event is shown in Figure 5b. This is a heavy summer storm of 4750 litres runoff which mixed and washed out most of the gullypot contents.

In the early stages of the storm the pH, dissolved oxygen and redox potential changes are typical of gullypot mixing. The next 30 min is characterised by a washing of the gullypot with rainwater which causes a drop in pH and conductivity and an increase of redox potential and dissolved oxygen. During the subsequent heavy rainfall further reducing sediment is remobilised, causing a drop in redox potential and a corresponding increase of pH. This shows that the residual buffering capacity of the gullypot may

CHALMERS GULLYPOT 11 JULY 1984

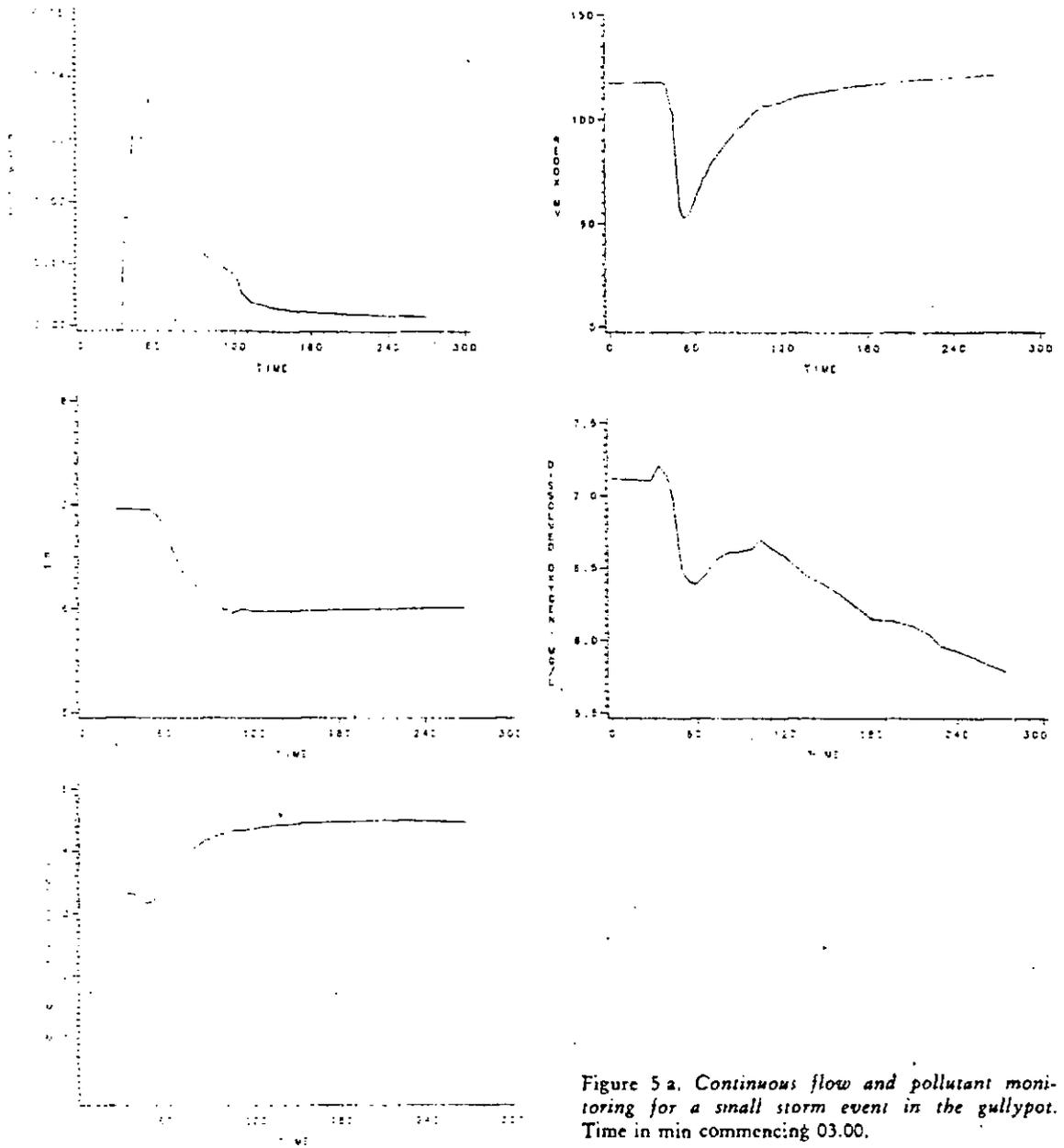


Figure 5 a. Continuous flow and pollutant monitoring for a small storm event in the gullypot. Time in min commencing 03.00.

be increased during intense rainfall due to further bottom sediment mobilisation.

Rainwater is saturated with dissolved oxygen and so dissolved oxygen concentration remains high until the storm event is over. The peak concentrations correspond with high gullypot water inflows. After the rainfall a slow decrease

of dissolved oxygen concentration is observed which may be related to bacterial respiration.

**Conclusion**

The continuous on-line system allows detailed monitoring of selected pollutants in stormwater.

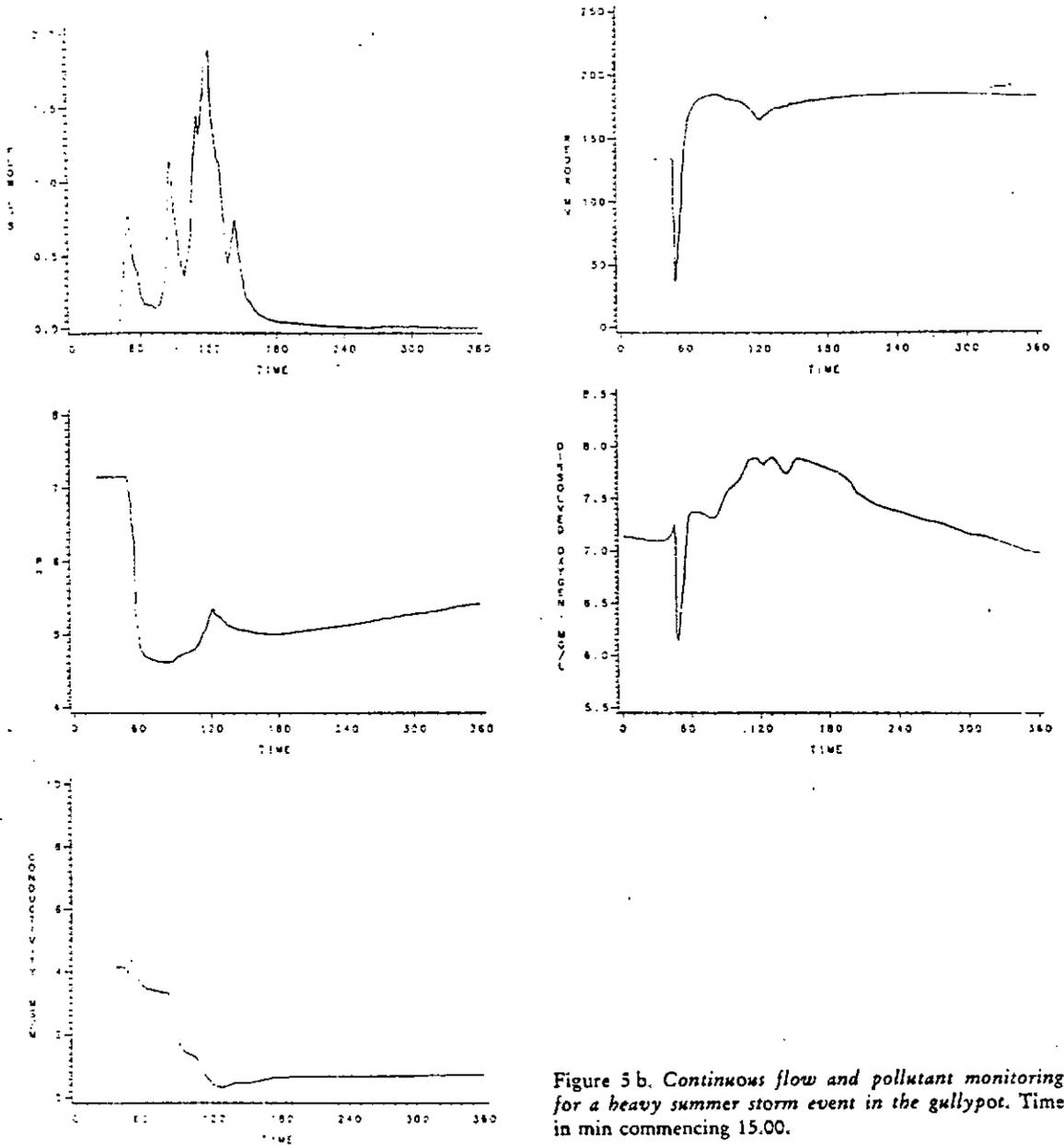


Figure 5 b. Continuous flow and pollutant monitoring for a heavy summer storm event in the gullypot. Time in min commencing 15.00.

The system requires calibration once a week and should be checked more frequently in cases of suspected blockage by solids.

It is suggested that the system might find wider fields of application in water research projects involving the continuous monitoring of river and estuarine water, of combined and separate sewer discharges, or even of industrial effluent discharges.

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