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**DISTRIBUTION OF HEAVY METALS ON
SEDIMENTS UNDER DIFFERENT FLOW
CONDITIONS**



आपो हि ष्टा मयोभुवः

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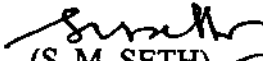
PREFACE

The water of rivers and freshwater lakes plays an important role in all the development programmes of the country. They also serve as a source of water supply for domestic and industrial purposes and also for agriculture, fisheries and power development. The same water resources are also utilized for the disposal of industrial wastes and sewage leading to water pollution. In recent years, with the rapid development of industries, water pollution is assuming serious concern. There is a growing need to understand the implications of the discharge of the wastewater into streams.

Heavy metals particularly are of enhanced importance in industry. Many rivers in densely populated areas contain large amount of metals. Metal concentration in rivers are able to oscillate in wide ranges. One important fact in varying the concentration in water is the influence of metals bound to sediments. The heavy metal load of sediments often reaches such high levels that a sudden desorption would be a great danger. Therefore, sorption and desorption processes influence water quality to a great extent.

Keeping the above points in mind study entitled 'Distribution of heavy metals on sediments of river Hindon under different flow conditions' was taken up with a view to demonstrate the role of sediments in transport of heavy metals. The river carries pollution load from industrial towns and agricultural areas of western Uttar Pradesh and is one of the important tributaries of river Yamuna.

The report has been prepared by Dr. C. K. Jain, Scientist 'E', under the work-programme of Environmental Hydrology Division for the year 1999-2000.


(S. M. SETH)

DIRECTOR

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ABSTRACT

The river Hindon is subjected to varying degree of pollution caused by numerous untreated waste outfalls of municipal and industrial effluents. The main sources, which create pollution in river Hindon include municipal waste of Saharanpur, Muzaffarnagar and Ghaziabad districts and industrial effluents of sugar, pulp and paper, distilleries and other miscellaneous industries through tributaries as well as direct outfalls. The flow in the river varies widely and is controlled by the release of water from Upper Ganga Canal through Khatauli and Jani escapes.

In this study we have analyzed the distribution of heavy metals (Cu, Zn, Fe, Mn, Co, Cd, Cr, Pb, Ni and Al) in water, suspended and bed sediments of river Hindon polluted by municipal, industrial and agricultural effluents, which flows through the city of Saharanpur, Muzaffarnagar and Ghaziabad districts. The heavy metal concentrations in water were observed to depend largely on the amount of flowing water and are negatively correlated with flow.

Sediment analysis indicates that the large amount of heavy metals are associated with organic matter, the fine-grained sediment fraction and Fe/Mn hydrous oxides. A high positive correlation of most of the metal ions in sediments with iron, manganese and organic matter indicate that these constituents play a major role in transport of metal ions.

The heavy metal concentrations generally increased with the decreasing particle size of the sediments. The maximum concentration was observed in 0-75 μm sediment fraction. Lower metal concentrations in bed sediments during post-monsoon season established that monsoon had a slight effect on status of metals in sediments by causing renewal and mobilization of metals from the sediments.

1.0 INTRODUCTION

Urban settlements and growing industrial development, combined with rapidly increasing demand for water, are the main factors causing water quality management problems. Ninety six percent of water pollution problems in India are due to indiscriminate discharge of municipal wastes (Chaudhary, 1981). These wastes being biodegradable produce a series of directional but predictable changes in water bodies. Industrial effluents are also responsible for pollution of water bodies and the effects produced by them may be more serious as nature is often unable to assimilate them. Agriculture is also responsible for degrading the river water quality by generating runoff from animal husbandry units, which contain predominantly organic compounds from the use of mineral fertilizers and chemical pesticides.

The presence of heavy metals has long been used to determine the extent of pollution in a given area. Heavy metals can be dispersed to the aquatic environment through a variety of sources including industrial effluents, agricultural and urban runoff and domestic wastes. Many different metals have been widely used in environmental pollution studies, particularly Hg, Cu, Zn, Pb, Cr and Cd.

Many rivers in densely populated countries contain large amount of metals. Metal concentrations in rivers are able to oscillate in wide ranges. One important fact in varying the concentrations in water is the influence of metals bound to sediments. The heavy metal load of sediments often reaches such high levels that a sudden desorption would be a great danger (Salomons and Forstner, 1984). Therefore sorption and desorption processes influence the water quality. Occasionally transport of sediments-rich water results in increased heavy metal concentration in rivers. Another important factor in increasing metal concentration is the existence of complexes such as humides or other organic substances.

Heavy metals are not biodegradable and enter the food chain through a number of pathways causing progressive toxic actions due to the accumulation in different organs during a life

span and long term exposure to contaminated environments. Despite the presence of trace concentrations of Cr, Mn, Co, Cu and Zn in the aquatic environment, which is essential to a number of life processes, high concentrations of these metals become toxic.

In recent years, the fluxes of the many trace elements from terrestrial and atmospheric sources to the aquatic environment have increased considerably (Forstner and Whitmann, 1981). Pathways by which trace elements can enter the aquatic environments include atmospheric deposition and point and non-point source releases to surface water. Point sources of trace element include municipal sewage sludge, effluent to surface waters from coal-fired power plants, releases directly to water courses from industrial uses, and in some areas, acid mine drainage. Non-point sources of trace elements include natural weathering of geologic materials and anthropogenic sources such as runoff from manure and chemical fertilizers from farm fields and irrigation return flow. Industrial uses and sources include agriculture (As, Cu, Hg, Pb, Se and Zn), electrical power (As, Cd, Cu, Hg, Pb, Ni, Se and Zn), metallurgy (As, Cd, Cr, Cu, Hg, Pb, Ni and Zn), and wood and pulp (As, Cd, Cr, Cu, Hg and Pb). Elevated levels of these trace metals in natural water systems pose a severe threat to the aquatic environment (Forstner and Whitmann, 1981).

Zhang and Huang (1993) studied eight dissolved trace metals (Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn) in the most turbid large world river Huanghe, China. These metal concentrations occurred at levels lower than the frequently reported in China. There were correlations between the metals and major elements in the river indicating the significance of weathering and erosion in controlling water chemistry.

The increasing environmental problems due to acidification and metal contamination of streams require a more fundamental understanding of sediment dynamics and pathways for dissolved and particulate metal transport (Bencala et al., 1984; Moriarty and Hanson, 1988; Salomons and Forstner, 1984). A commonly used approach to study in-stream reactions, deposition, erosion or resuspension is chemical mass balance (Yuretich and Batchelder, 1988; Latimer et al., 1988; Elder, 1985; Christophersen and Wright, 1981; Plummer and Back, 1980). This approach may be useful when dynamic and high variable relationships between physical and chemical mechanisms

on a larger scale within a given reach of a river must be understood.

Berndtsson (1990) established water budgets and chemical mass balances of some water quality constituents for a 5-km-long reach of the river Hoje in the south of Sweden and reported that half of the transported zinc is retained within the stream sediments. Large retention of pollutants to stream sediments, particularly heavy metals, also has been observed in other studies. Imhoff et al. (1980) studied the heavy metals in the Ruhr river and reported that about 31% of the total load of heavy metals to the Ruhr basin are retained in the stream sediments. Kartz et al. (1985) established mass balance for major constituents in precipitation and stream water and reported that dissolved solutes from precipitation input account for 12 to 19% of the total dissolved load in the stream water. Paces (1985) used mass balance models to estimate elemental budgets in Elbe river basin.

El-Shaarawi et al. (1983) studied the temporal trend of Niagara river with respect to pH, alkalinity, total phosphorous and nitrates using statistical approach. Dolon and El-Shaarawi (1989) studied Niagara and Detroit river containing myriad of point and non-point sources. They indirectly monitored these sources by upstream/downstream sampling at the head and the mouth of the rivers.

Numerous studies have demonstrated that the determination of metal concentrations in suspended and bed sediments is more sensitive than the dissolved concentrations as indicators of contamination in hydrologic systems (Salomons and Forstner, 1984; Luoma, 1990). For a limited reconnaissance survey of a large river system, sediment concentrations provide a better evaluation of the degree and the extent of contamination in the aquatic environment.

The continental contribution of heavy metals to the worlds ocean is quite large, as >97% of the mass transport of metals is associated with river sediments (Gibb, 1977). A variety of factors such as basin geology, physiography, chemical reactivity, lithology, mineralogy, hydrology, vegetation, land use pattern and biological productivity regulate the metal load of a river system (Garrel et al., 1975; Warren, 1981; Aurada, 1983). Due to the relative mobility of metals during

transport processes, sediment can reflect the present quality of the basin and the historical development of various hydrological and chemical parameters.

The metal contribution from Indian rivers, which carry 20% of the global supply of sediments to the oceans (Subramanian, 1979) has not been properly assessed as smaller basins such as the Yamuna, Sone, Gandak and Kosi carrying 64×10^6 , 17×10^6 , 30×10^6 , and 68×10^6 t year⁻¹ of sediment, respectively, have not been studied. Previous studies by Martin and Meybeck (1979) and Sarin et al. (1979) are based on a few samples from large rivers only. Subramanian et al. (1985) attempted to estimate an average chemical composition of Indian river sediments based on large rivers. Borole et al. (1982) and Subramanian et al. (1988) have reported metal concentrations and their non-conservative behaviour in estuarine sediments on the west and east coast of India. Recent geochemical studies of some basins (Subramanian et al., 1987; Biksham and Subramanian, 1988; Ramanathan et al., 1988; Subramanian and Jha, 1988; Ramesh and Subramanian, 1989) have yielded additional data to improve and update information on the metal contribution of Indian rivers to the adjacent ocean.

The Yamuna contributes 64×10^6 t year⁻¹ of suspended sediments and 42×10^6 t year⁻¹ of dissolved load to the Ganges (Jha et al., 1988). The associated metal load after mixing with the Ganges is likely to influence its downstream metal budget. Bed sediments of Yamuna have higher concentrations of metals than other tributaries. Sediment grain size, mineralogical difference and varying amounts of anthropogenic contributions may be the prime factors controlling metal variation. Subramanian and Sitasawad (1984) reported that annually, 86 t Ni, 64 t Cr, 61 t Pb, 45 t Fe and 36 t Zn, derived from industrial effluents and city wastes are disposed into the river Yamuna in the vicinity of Delhi alone.

Jha et al. (1990) studied the metals in suspended, bed and core sediments of river Yamuna and found that the variation of metals in sediments are due to the varying proportions of grain size and mineral content. The mobility of metals is regulated by the chemically mobile fraction of sediments. Fe, Mn and Pb are dominant in the oxide fraction while Cu and Zn are concentrated in the organic and carbonate fraction. For Yamuna river sediments, organic matter is important in

the accumulation of metals. River sediments in the vicinity of Delhi show an increase in sorption of metals. Foster and Hunt (1975) also demonstrated the importance of organic matter in the accumulation of metals by chelation

Clay minerals also control the level of metals in the sediment-water system due to their greater cation exchange capacity promoting the adsorption of positively charged metal ions (Raymahashay, 1987). Although illite is predominant throughout the Yamuna basin, the tributaries contain relatively more montmorillonite, which is known to have the highest exchange capacity among clay minerals (Forstner and Whitmann, 1981).

It has been clearly shown that the presence of heavy metals is affected by the particle size and composition of sediments (Krumlgalz, B. S., 1989; Hiraizumi et al., 1978; Ogura et al., 1979; Kristensen, 1982; Yamagata and Shigematsu, 1970; Mizobuchi et al., 1975; Asami and Sampei, 1979; Thomson et al., 1984; Thorne and Nickless, 1981). The different fraction of particle size may give different heavy metal concentrations in the same sediment samples. Yamagata and Shigematsu (1970) also reported that heavy metals should not be analyzed simply in the total sediment, but it should be carried out with due consideration of the particle size itself.

Sakai et al. (1986) analyzed the distribution of Mn, Zn, Cu, Pb, Cr and Cd in water and sieved sediment samples of Toyohira river, Japan. Since there was a close relationship between metal changes in water and sediments, the marked distribution trend of Mn, Zn and Cd was almost the same for both. The heavy metal concentrations generally increased with decreasing particle size of sediments. Seasonal changes in concentrations of particles of smaller size, moreover, were greater than changes among the larger particles.

Sabri et al. (1993) determined the concentrations of Cd, Cu, Co, Fe, Zn, Mn, Pb and Ni in water, suspended solids and surficial sediments of the river Tigris at Samarra impoundment during high and low river discharge period and reported that the metal concentrations in water were within the prescribed standards. Variations in the concentration of heavy metals in suspended solids were interpreted to be due to local difference in the current velocity and the distance from the

shoreline (from sewage source). The concentrations of most of the examined elements in the surficial sediments (except for Mn and Fe) were lower than those in the suspended solids. Results stress the importance of the suspended solids in transportation of heavy metals in the river.

Combest (1991) evaluated sediment trace metals in White Rock Creek watershed located in Dallas and Collin Counties of north central Texas, in relation to sediment sorption characteristics and down stream metal trend. Analysis determined that downstream trace metals trends, as related to the watershed's metal inputs could not be recognized by analyzing the <2 mm (<sand) sediment size fraction. Conversely, the trace metal concentrations were found to be distinctly related to sediment characteristics.

Rice (1999) during National Water Quality Assessment program of US Geological Survey collected 541 stream bed sediments from 20 study area and studied the interrelationship among the different metals. He reported that the sum of the concentrations of copper, mercury, lead and zinc was well correlated with population density of urban settings. He also examined four different methods of accounting for background/baseline concentrations.

Murray et al. (1999) assessed the metal enrichment of the bed sediment of the lower reaches of the Rouge river. The studied metals (Cr, Cu, Fe, Ni, Pb, Zn) were predominantly present in the sequentially extracted reducible and oxidisable chemical phases with small concentrations from residual phases. In size fractionated samples, these metals increases with decreasing particle size with the greater contribution to this increase from oxidisable phase.

Phillips and Hershelman (1996) studied the temporal trends in metal concentrations in sediments near a large wastewater outfall in southern California and found that the change in effluent concentrations of cadmium, copper, chromium, nickel and zinc explained 48% to 62% of the variance in the corresponding metal ion concentrations in the sediments immediately adjacent to the outfall. However, correlations between effluent and sediment metal concentration were generally weaker at greater distance from the outfall.

Coquery and Welbourn (1995) studied the relationship between metal concentration and organic matter in sediment core samples of Bentshoe lake, situated in south-central Ontario, Canada. They inferred that a significant positive correlation was found between metal concentrations in sediment and organic matter content. Organic matter in sediment tends to decrease the availability of metals to sediment dwelling organisms because of the formation of complexes between metals and organic matter (Campbell et al., 1988).

In western Uttar Pradesh rapid industrial and agricultural growth has taken place during last few decades. This is likely to become manifold in near future particularly in areas like Saharanpur, Muzaffarnagar, Meerut and Ghaziabad where necessary industrial nucleus already exists. A variety of industries have already been set up in this area such as paper and pulp, sugar, chemicals, rubber, plastics, food-processing, small scale industries and cottage industries etc. Most of these industries are discharging their wastes and effluents into the nearby water course without considering its consequences. Verma et al. (1974) studied the characteristics and disposal problems of various industrial effluents with reference to Indian standards. In addition to this, the municipal waste of Saharanpur, Muzaffarnagar, Meerut and Ghaziabad districts are also being discharged to the nearby rivers. On account of these outfalls of municipal and industrial wastes into the rivers, the water is subjected to varying degree of pollution.

The river Hindon, an important tributary of river Yamuna, carries pollution load from industrial towns and agricultural areas of western Uttar Pradesh. The river originates from Upper Shivaliks (Lower Himalayas) and flows through four major districts namely Saharanpur, Muzaffarnagar, Meerut and Ghaziabad in western Uttar Pradesh and finally joins river Yamuna downstream of Delhi.

Some preliminary studies have been conducted on some selected stretches of river Hindon dealing with the pollutional aspects of the river (Rao, 1965; Verma and Mathur, 1971; Handa, 1983a,b; Joshi, 1987; Kumar and Mathur, 1991; Seth and Singhal, 1994; Kumar, 1994; Khare, 1994; Report on Hindon Monitoring Project, 1996; Kumar, 1997).

Verma et al. (1980) conducted detailed limnological studies of Hindon river in relation to fish and fisheries and reported that quality of the river water is not suitable for propagation of fish culture and related aquatic life. Singhal et al. (1987) studied the influence of industrial effluents on water quality of river Hindon. Seth (1991) carried out studies on hydrological aspects of waste disposal in the Upper Hindon basin while Kumar (1993) have investigated the bioaccumulation and concentration of toxic metals (Cd, Pb and Zn) in aquatic flora and fauna alongwith the impact of physico-chemical conditions in the river. Lokesh (1996) studied the fate of some heavy metals in water and sediments of the Hindon river. In an earlier report detailed hydro-chemical studies of river Hindon have been reported (Jain and Sharma, 1998).

Recently, detailed studies on water and sediments of river Kali, a tributary of river Hindon, have also been carried out in the Water Quality Laboratory of National Institute of Hydrology, Roorkee (Jain, 1996; Jain and Ram, 1997a,b; Jain et al., 1997, 1998a,b). It is reported that the river is highly polluted due to the numerous untreated municipal and industrial effluents of Muzaffarnagar district. The discharge of municipal and industrial wastes at regular intervals does not allow any self purification to occur. The important characteristic associated with the pollution of the river is the depletion of oxygen over a stretch of about 25 km. The mass balance conducted for some water quality constituents shows that changes found in load along the river may be mainly due to the contribution of non-point sources of pollution.

The present study was carried out with the objective to study the distribution of heavy metals in water, suspended sediments and bed sediments of river Hindon under different flow conditions. The role of sediments in the transport of heavy metals has also been investigated. The data was collected for a period of one year from April 1999 to March 2000 on monthly basis and results have been discussed in this report.

2.0 STUDY AREA

The Hindon basin is a part of Indogangetic Plains, composed of Pleistocene and subrecent alluvium and lies between latitude 28° 30' to 30° 15' N and longitude 77° 20' to 77° 50'. The river Hindon originates from Upper Shivaliks (Lower Himalayas) and flows through four major districts, viz., Saharanpur, Muzaffarnagar, Meerut and Ghaziabad in western Uttar Pradesh and Joins river Yamuna downstream of Delhi at Tilwara. (Fig. 1).

2.1 Physiography

Physiographically the area is generally flat except Siwalik hills in the north and north east. The area is devoid of relief features of any prominence except from deep gorges cut by nalas and rivers flowing through the area. River Ganga in the east and river Yamuna in west bound the river.

2.2 Drainage

Regarding the drainage of the area, the rivers generally flow from north to south. These rivers during most of the non-monsoon season carry water drained into them from ground water storage. Some of the important rivers of the area are the Ganga, Yamuna, Hindon, Krishna, and the Kali. Apart from these rivers, the Western Ganga Canal and Eastern Yamuna Canal also drain the area.

2.3 Climate

The climate of the region is moderate subtropical monsoon type. Significant diurnal variations in hydrometeorological parameters like precipitation, temperature and relative humidity exist. The temperature varies from 8°C in winter to 40°C in summer. The average annual rainfall is

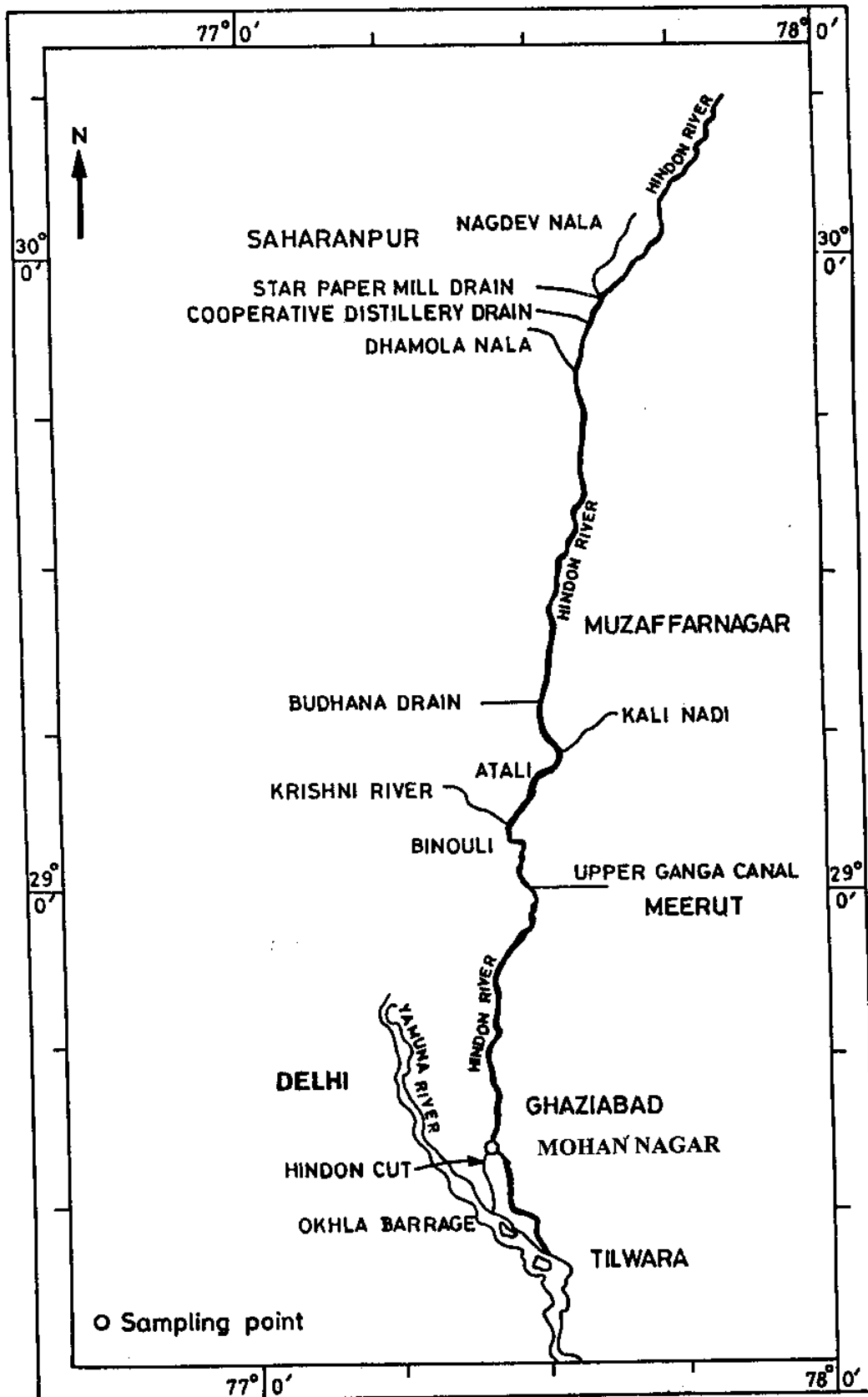


Fig.1 Study area showing the location of sampling point.

about 1000 mm, major part of which is received during monsoon period.

2.4 Geology

The area under study is a part of Indogangetic plain, which is mainly composed of pleistocene and subrecent alluvium brought down by river action from the Himalayan region. The soil type of the basin is alluvial. Lithologically, it mainly consists of clay, silt and fine to coarse sand. The deposits of sand beds of varying thickness are the main source of ground water in the area. The soils are very fertile for growing wheat, sugar cane and vegetables. However, along the sandy river coarse, fruit orchards are also common.

2.5 Landuse

The major landuse in the basin is agriculture. The basin is densely populated because of the rapid industrialization and agricultural growth during last few decades. Several industries related to paper, sugar, distillery and many small scale cottage industries related to electroplating, paper board, food processing, milk products, chemicals and rubber etc., existing in the western part of U.P., release their waste effluents into the river through various open drains.

2.6 Source of Pollution

The main sources, which create pollution in river Hindon include municipal waste of Saharanpur, Muzaffarnagar and Ghaziabad districts and industrial effluents of sugar, pulp and paper, distilleries and other miscellaneous industries through tributaries as well as direct outfalls. In non-monsoon months the river is completely dry from its origin upto Saharanpur township. The effluents of Nagdev nala and Star Paper Mill at Saharanpur generate the flow of water in the river. The municipal waste generated from the Saharanpur city is discharged to the Hindon river through Dhamola nala. The industrial effluent from Cooperative Distillery also joins the river in this stretch.

The river Kali meets river Hindon on its left bank near the village of Atali, which is carrying municipal wastewater and effluents of industries located in the Muzaffarnagar city. Another tributary called Krishni meets Hindon on its right bank at village Binouli in Meerut district and carrying the waste water from sugar mill and distillery. In Ghaziabad district, downstream of Karhera village, majority of flow of river is diverted to Hindon cut canal at Mohan Nagar which outfalls into river Yamuna upstream of Okhla barrage. Thereafter river Hindon receives wastewater through Dhasna drain at village Bisrakh in Ghaziabad district. Dhasana drain is carrying the wastewater of municipal as well as industrial establishments in Ghaziabad. River Hindon further downstream flows through Kulesara and joins river Yamuna at village Tilwara.

2.7 Sampling Station

A general plan of the river system with respect to different outfalls of municipal and industrial effluents in river Hindon is shown in Fig. 1. The location of main sources of pollution has also been indicated in the same figure. The water and sediment samples were collected from the Hindon river at Mohan Nagar. The sampling site is located just downstream of Hindon bridge at Mohan Nagar. Lot of human activities (washing and dying of cloths, disposing of ash of burnt bodies alongwith flowers and other offerings) are quite common upstream of this site. The river is quite wide at this place. The station is important since the water regulatory works (barrage and canal diversion point) are situated here.

3.0 EXPERIMENTAL METHODOLOGY

The water samples were collected in polyethylene bottles from 1/3, 1/2 and 2/3 width of the river using standard water sampler (Hydro Bios, Germany) and then mixed together to obtain a composite sample. . All the samples were collected from the upper 15 cm of the water surface and stored in polyethylene bottles fitted with screw caps. The sample bottles were soaked in 10% HNO₃ for 24 h and rinsed several times with double distilled water prior to use. The water samples were filtered through 0.45 µm membrane filter to obtain samples for dissolved metal estimations and preserved with ultra pure nitric acid to bring down the pH to <2.0. The samples thus preserved were stored at 4°C in sampling kits and brought to the laboratory for trace element analysis. The water samples for total metal analysis were preserved using ultra pure nitric acid and then digested on a hot plate. The discharge was measured using stage-discharge relationship.

Suspended sediments were also collected from 1/3, 1/2 and 2/3 width of the river by filtering river water samples through 0.45 µm membrane filters and then mixed together prior to analysis. Bed sediment samples were collected by an Ekman grab sampler from the bed of the river, dried at 70°C and sieved to obtain different particle fractions (0-75, 75-150, 150-200, 200-250, 250-300, 300-425 and 425-600 µm) using dry sieving method and stored in polyethylene bags till further processing. The extraction of sediments was carried out using acid mixture (HNO₃ + HClO₄). Organic matter in the sediment was determined by wet oxidation – redox titration method using an acid dichromate solution. The reported data are the sum of soluble and insoluble organic carbon.

All chemicals and standard solutions used in the study were obtained from Merck, India/Germany and were of analytical grade. De-ionized water was used throughout the study. All glass wares and other containers were thoroughly cleaned and finally rinsed with double distilled water several times prior to use. Trace element analysis was carried out using Perkin Elmer Atomic Absorption Spectrometer (Model 3110). Operational conditions were adjusted to yield optimal determination. Quantification of metals was based upon calibration curves of standard solutions of metals.

4.0 RESULTS AND DISCUSSION

Heavy metals added to a river system by natural or manmade sources during their transport are distributed between the aqueous phase, suspended and bed sediments. The fraction in the sediment is expected not to have direct adverse effects, if the metal ions are tightly bound to it and subsequently get settled at the bottom in course of time. This state of affairs is maintained until there is remobilization from the sediment due to changing conditions in the system. Thus, in the natural conditions of river water, suspended load and sediments have the important function of buffering higher metal concentrations of water particularly by adsorption or precipitation. Therefore, the study of sediments and their sorptive properties can provide valuable information relating to the tolerance of the system to the added heavy metal load and may determine the fate and transport of pollutants in the aquatic environment.

The Hindon river is one of the important tributaries of river Yamuna. The upper part of the Hindon river basin in Saharanpur district has a large number of industries related to paper, milk products, distillery and many small scale cottage industries related to electroplating, paper board, chemicals, and rubber, etc. The waste effluents generated from these industries are being released on lowlands and tributaries of the Hindon river system passing through the area. Much of these wastes apparently contaminate the receiving water as can be felt from the foul smell and anaesthetic colour especially in the stretches to the downstream of the outfalls of waste effluents.

The main effluent discharge in the upper part of the river system is from Star Paper Mill, Saharanpur. Beside this, the river has two drains in its upper portion, viz., Nagdev nala and Dhamola nala, which join the river Hindon near the village of Ghogreki and Sadhauri Haria, respectively. The municipal wastewater generated from the Saharanpur city is discharged to the Hindon river through Dhamola nala. In addition, the wastes from several small units such as textile factory, sugar factory, cigarette factory, cardboard factory and laundries etc. also transfer their wastes to the river Hindon through Dhamola nala. The industrial effluent from Cooperative distillery also joins the river in this stretch.

In the middle portion of the basin, river Kali carrying the municipal and industrial effluents of Muzaffarnagar district join the Hindon river near the village of Atali. River Krishna receiving wastes from sugar mill and distillery joins river Hindon near the village of Barnawa. Besides these, some local drains from villages and towns also join the river. There are no notable waste outfalls in the lower portion of the study area.

The characteristics of the various waste effluents/tributaries and their impact on river water quality have been discussed in an earlier report (Jain and Sharma, 1998). Table 1 lists some of the major heavy metals employed in various industries.

4.1 Heavy Metal Concentrations in Water

The distribution of heavy metals in dissolved, total and particulate matter and their seasonal changes is given in Fig. 2. The concentration of dissolved metals decreased in the monsoon months due to dilution effect of rainfall. The lower concentration in dissolved metals in the month of February/March is due to the release of substantial amount of water from Ganga canal. The heavy metal concentrations in water were observed to depend largely on the amount of flowing water. Fig. 3 shows plots of the relationships of dissolved metal concentration with flow and Table 2 gives the correlation coefficients among different metal ions and flow. In order to develop best relationship between metal ion concentration and flow, different relationships were tried and the best regression equation explaining the variation of concentration with flow are given in Table 3, alongwith respective coefficient of determination (r^2). As is evident from the values of coefficient of determination, the relationship is well defined for Cu, Cd and Ni and less well defined for Zn, Fe, Mn, Cr and Pb.

The heavy metal concentrations are negatively correlated with flow. This may be attributed to the dilution effect of rainfall and/or release of water from Ganga canal. The significant correlation coefficients of metal ions with iron and manganese indicates that the metal ions are controlled by Fe and Mn, which are the important geochemical components for the transport of metal

Table 1. Trace element employed in various industries

Industrie(s)	Cd	Cr	Cu	Fe	Hg	Mn	Pb	Ni	Sn	Zn
Pulp, Papermill, Paperboard, Building paper, Board mills		X	X		X		X	X		X
Organic chemicals, Petrochemicals	X	X		X	X		X		X	X
Alkalis, chlorine, Inorganic chemicals	X	X		X	X		X		X	X
Fertilizers	X	X	X	X	X	X	X			X
Petroleum refining	X	X	X	X			X	X		X
Basic steel works foundries	X	X	X	X	X		X	X	X	X
Basic nonferrous metal works, Foundries	X	X	X		X		X			X
Motor vehicle, Air craft plating, Finishing	X	X	X		X			X		
Flat glass, Cement, Asbestos products		X								
Textile mill products		X								
Leather tanning, Finishing		X								
Steam generation power plant		X								X

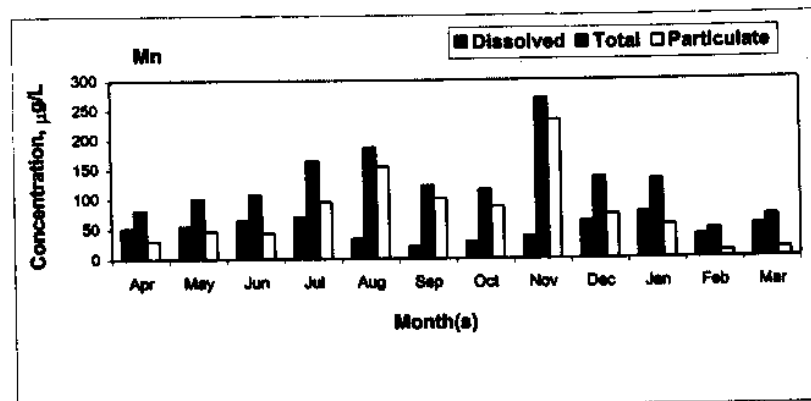
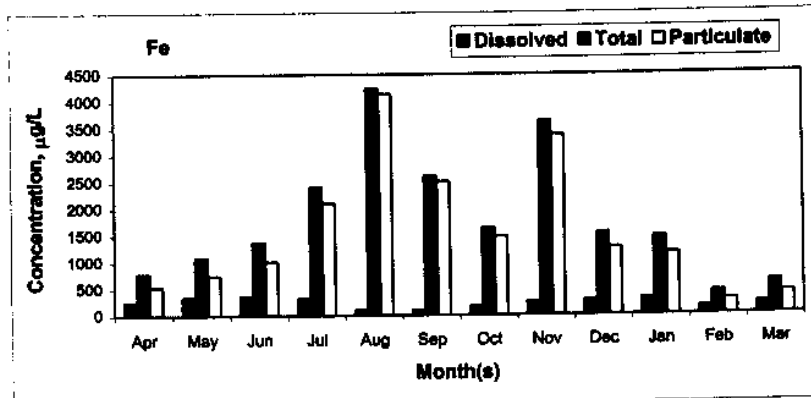
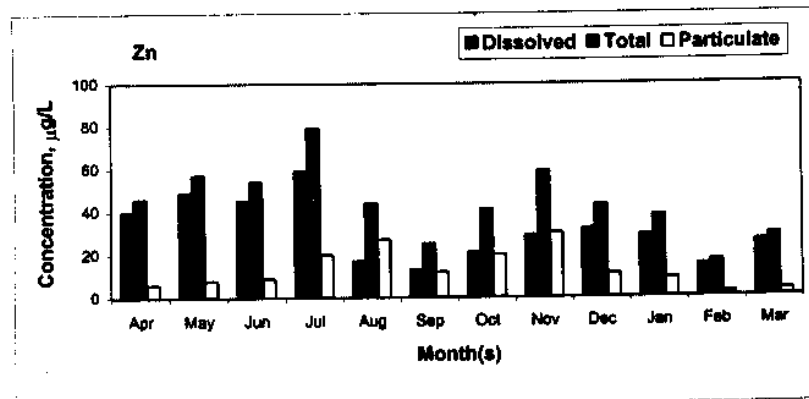
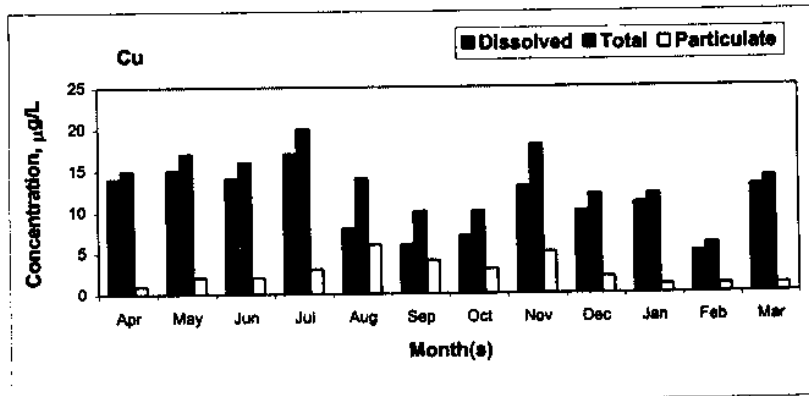


Fig. 2(a). Monthly variation of dissolved, total and particulate metal concentrations
- 17 -

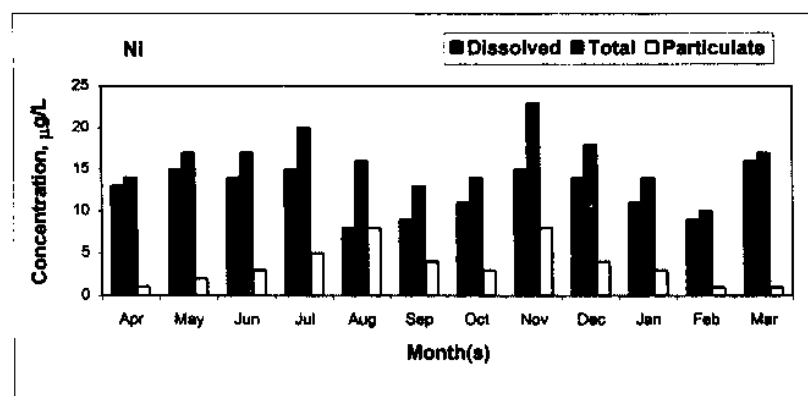
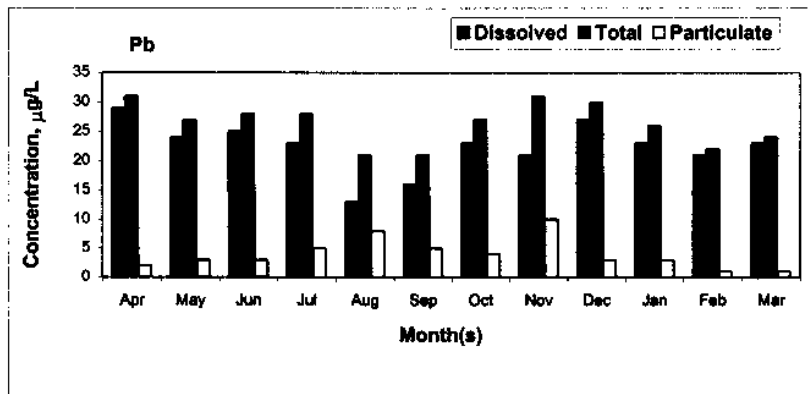
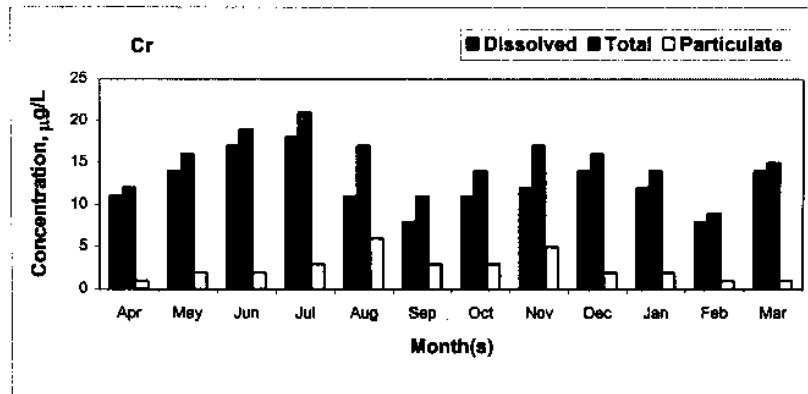
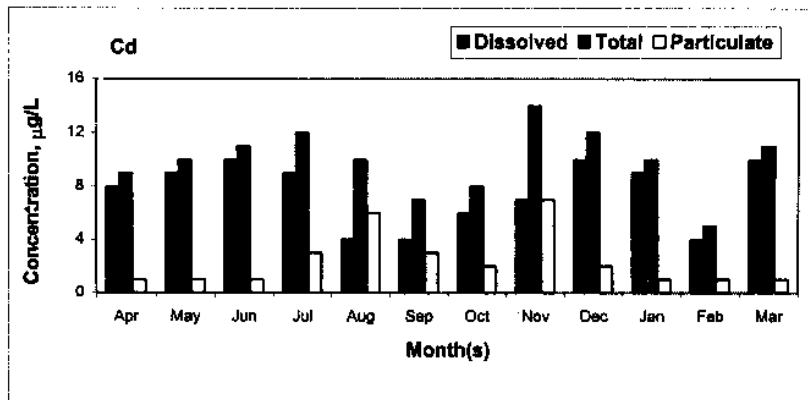


Fig. 2(b). Monthly variation of dissolved, total and particulate metal concentrations
- 18 -

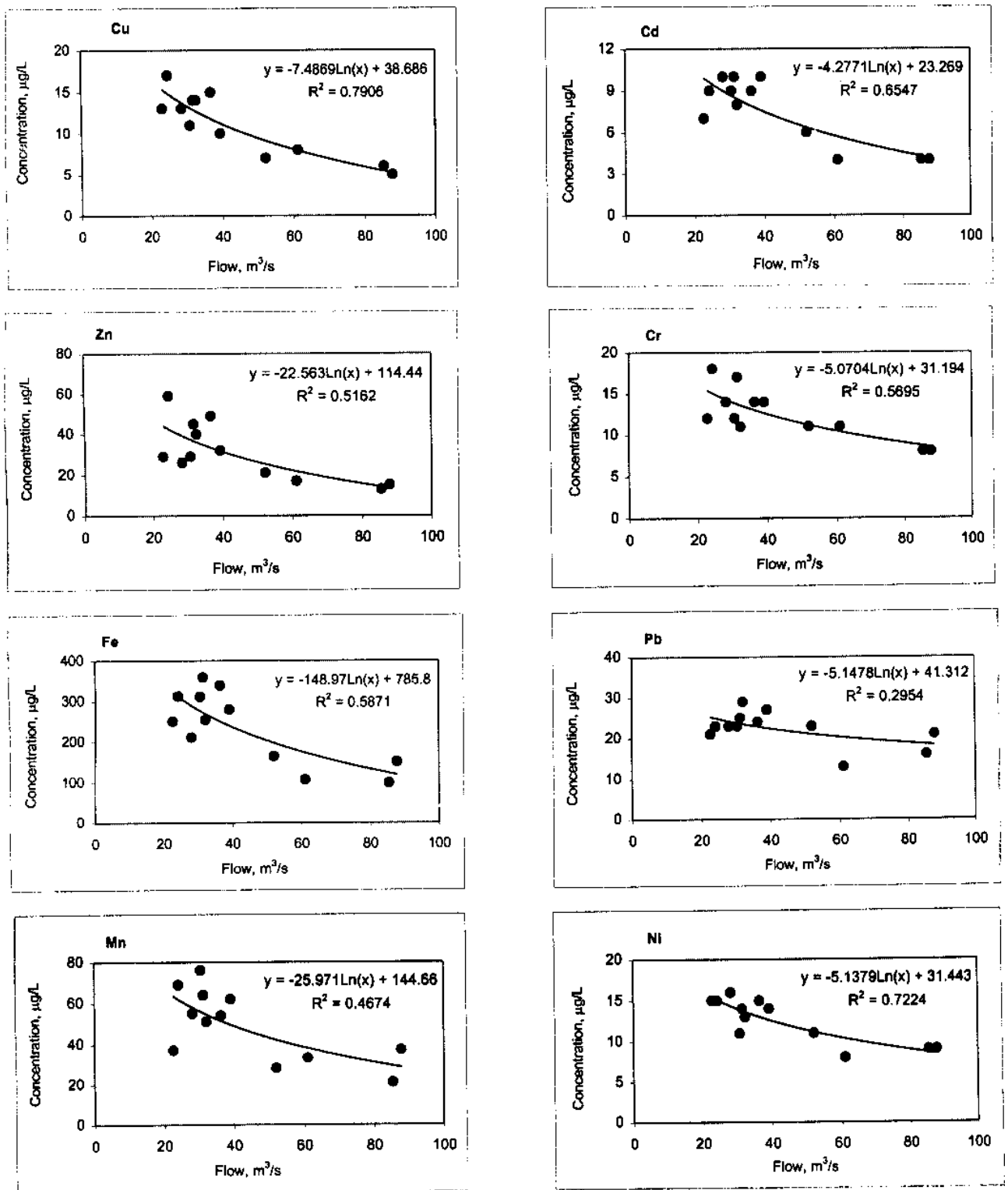


Fig. 3. Relationship between dissolved metal concentrations and flow

Table 2. Correlation coefficients among dissolved metal concentrations

	Flow	Cu	Zn	Fe	Mn	Cd	Cr	Pb	Ni
Flow	1.000								
Cu	-0.876	1.000							
Zn	-0.721	0.913	1.000						
Fe	-0.780	0.812	0.859	1.000					
Mn	-0.698	0.686	0.707	0.850	1.000				
Cd	-0.842	0.778	0.724	0.867	0.851	1.000			
Cr	-0.772	0.825	0.847	0.784	0.739	0.811	1.000		
Pb	-0.577	0.526	0.590	0.707	0.600	0.747	0.432	1.000	
Ni	-0.832	0.840	0.724	0.735	0.561	0.848	0.752	0.646	1.000

Table 3. Regression equations for different dissolved metals

Metal	Regression equation	Coefficient of determination
Cu	$y = -7.4869 \ln(x) + 38.686$	0.79
Zn	$y = -22.563 \ln(x) + 114.44$	0.52
Fe	$y = -147.97 \ln(x) + 785.8$	0.59
Mn	$y = -25.971 \ln(x) + 144.66$	0.47
Cd	$y = -4.2771 \ln(x) + 23.269$	0.66
Cr	$y = -5.0704 \ln(x) + 31.194$	0.57
Pb	$y = -5.1478 \ln(x) + 41.312$	0.30
Ni	$y = -5.1379 \ln(x) + 31.443$	0.72

y = Dissolved metal concentration; x = Flow

ions. The significant correlation coefficients ($r > 0.7$) among different dissolved metals also point out to the weathering effect.

The particulate fraction contains higher concentration of metal ions during monsoon months (Fig. 2). This may be attributed to simple sediment transport functions, whereby increases in flow are associated with increased water turbulence and sheer velocities. These result in an increased capacity to erode and transport particulates from the upstream catchments and the channel network. The particulate component contains highest concentration of iron and manganese as compared to other metals, which are the important component for the transport of metal ions. The relationships of particulate metal concentrations with flow are presented in Fig. 4. The particulate fraction did not show any pronounced trend with flow.

It is evident from the above discussion that the concentration of heavy metals in water is highly influenced by the flow of the water. Therefore, it is thought necessary to assess the pollution of the river relative to the metal concentrations, which are easily accumulated in suspended and bed sediments. Numerous studies have also demonstrated that the determination of metal concentrations in suspended and bed sediments is more sensitive than dissolved concentrations as indicators of contamination in hydrologic systems (Solomons and Forstner, 1984; Luoma, 1990).

4.2 Heavy Metal Concentrations in Suspended Sediments

The distribution of heavy metals in suspended sediments and their seasonal changes is shown in Fig. 5. The concentration of metal ions in suspended sediments decreased in the monsoon months due to dilution effect of rainfall. The lower metal concentrations in suspended sediments during monsoon season are attributed to the dilution of the contaminated sediments by uncontaminated sediments from the watershed and/or bed of the river.

The correlation coefficients developed among various metal ions in suspended sediments are given in Table 4. Negative correlations were observed between amount of suspended

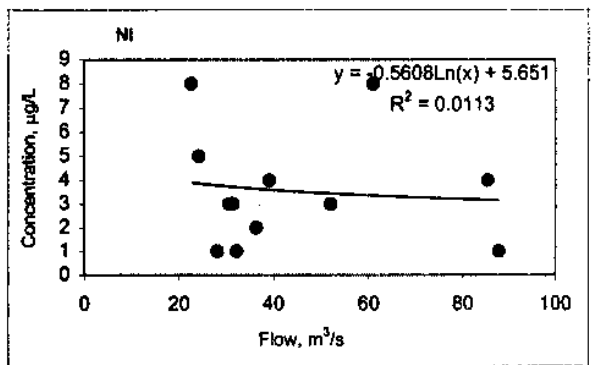
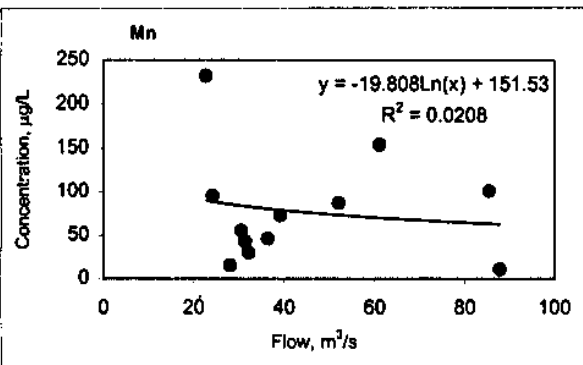
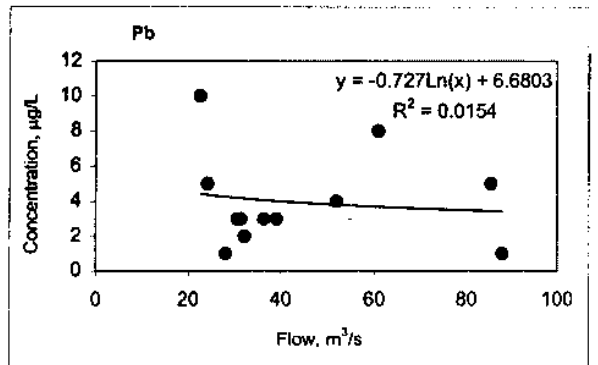
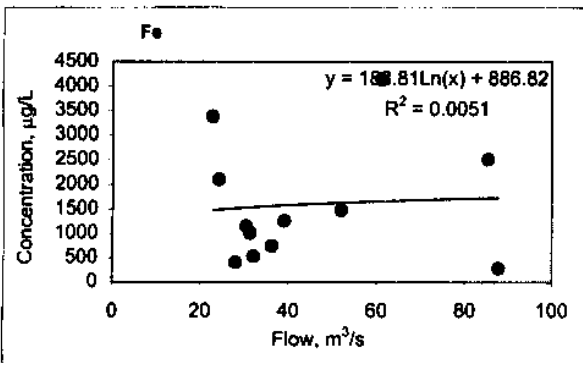
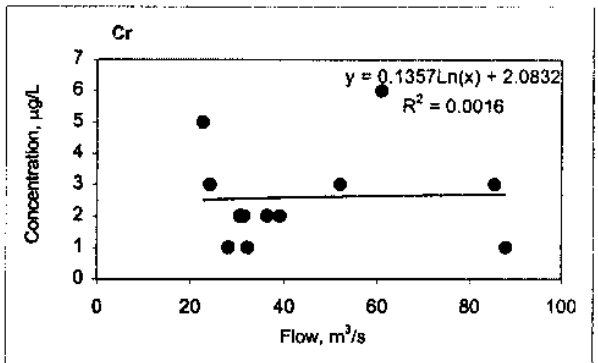
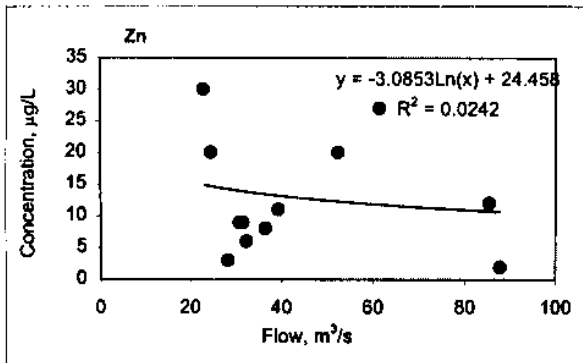
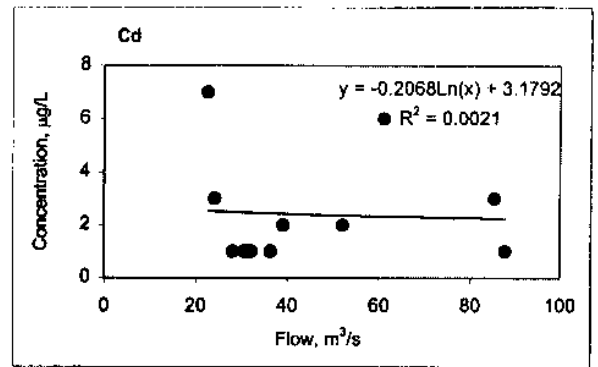
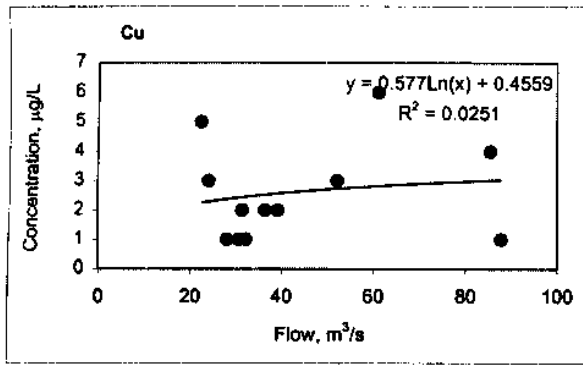


Fig. 4. Relationship between particulate metal concentrations and flow

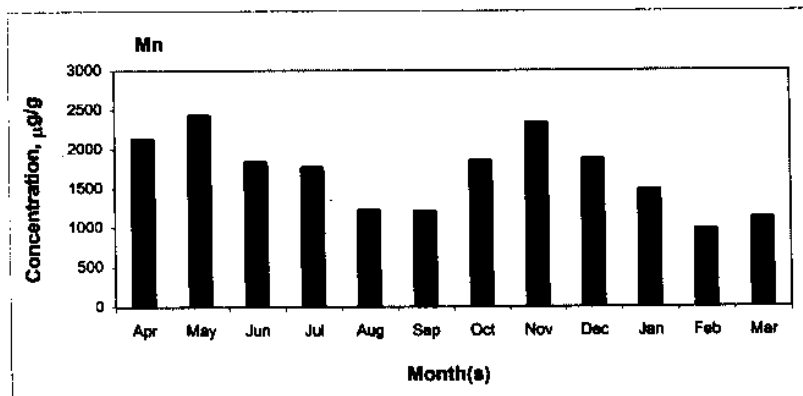
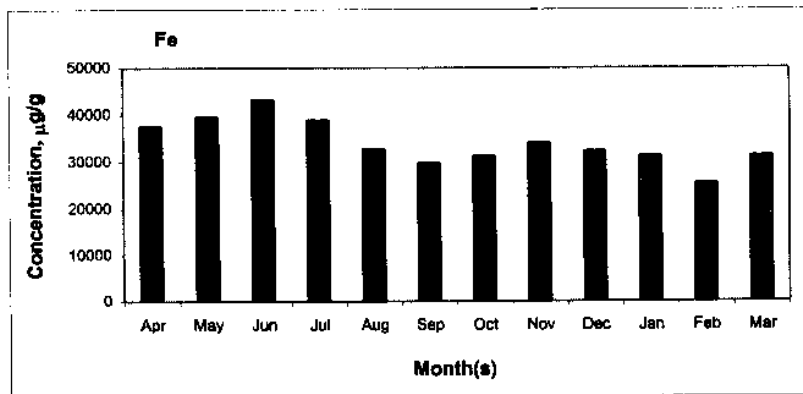
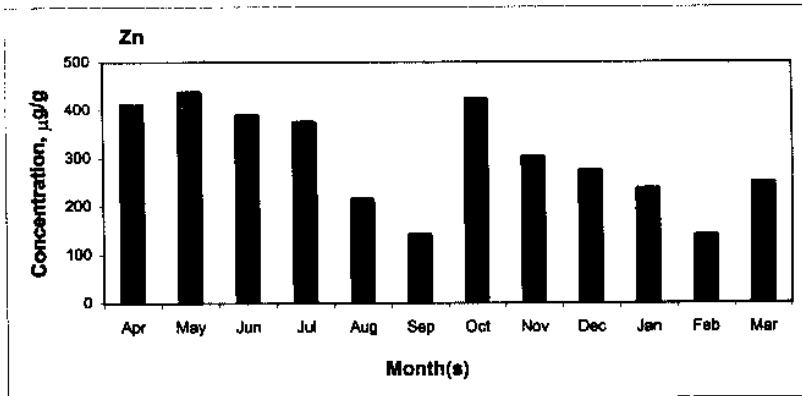
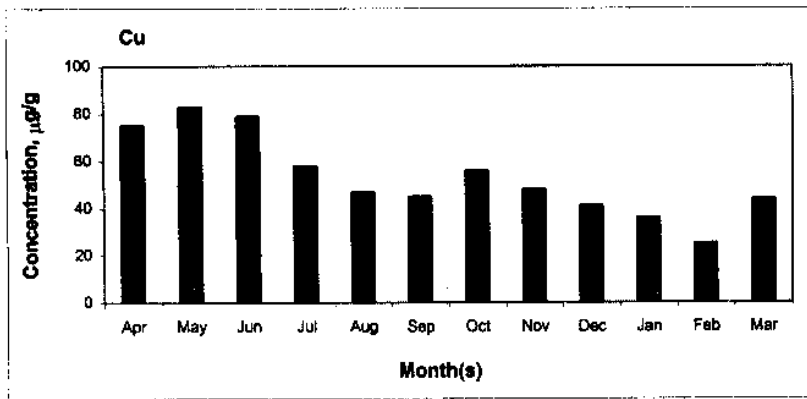


Fig. 5(a). Monthly variation of metal concentrations in suspended sediments

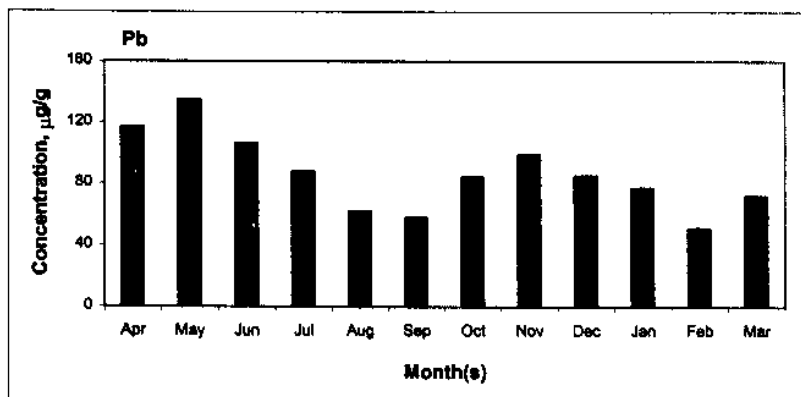
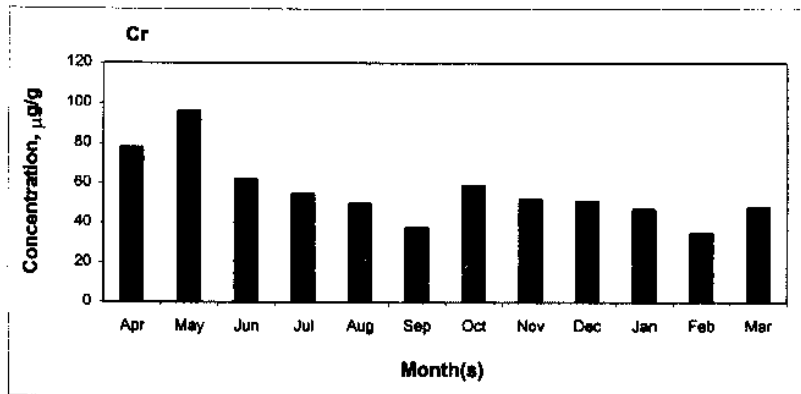
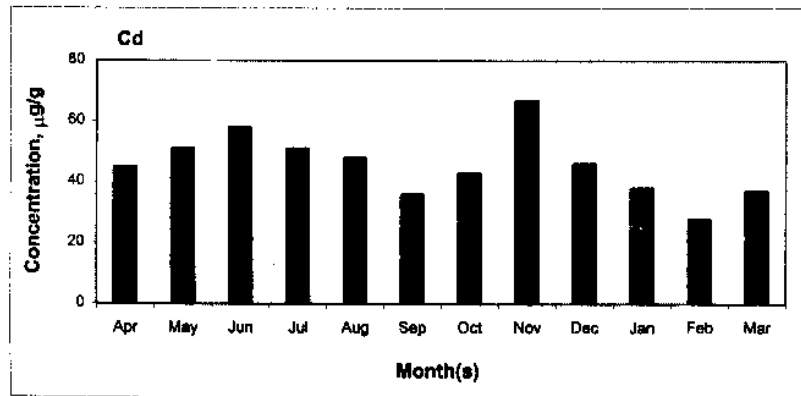
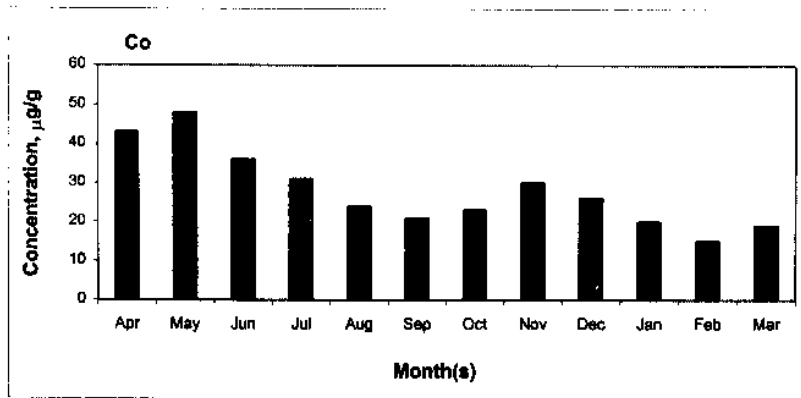


Fig. 5(b). Monthly variation of metal concentrations in suspended sediments

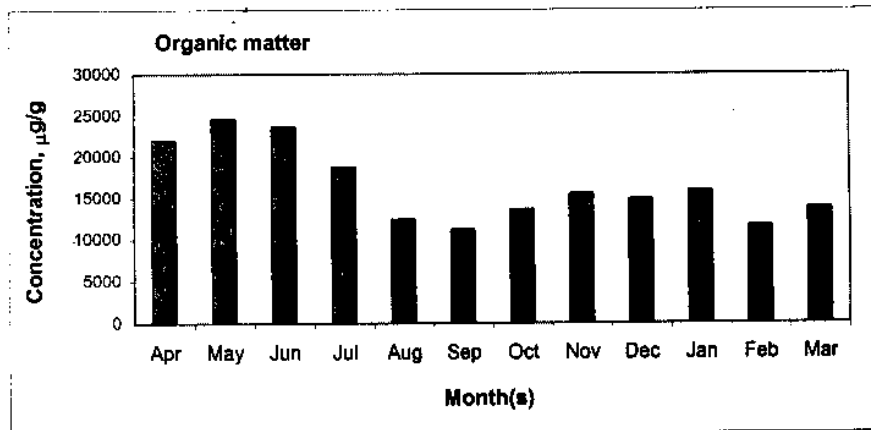
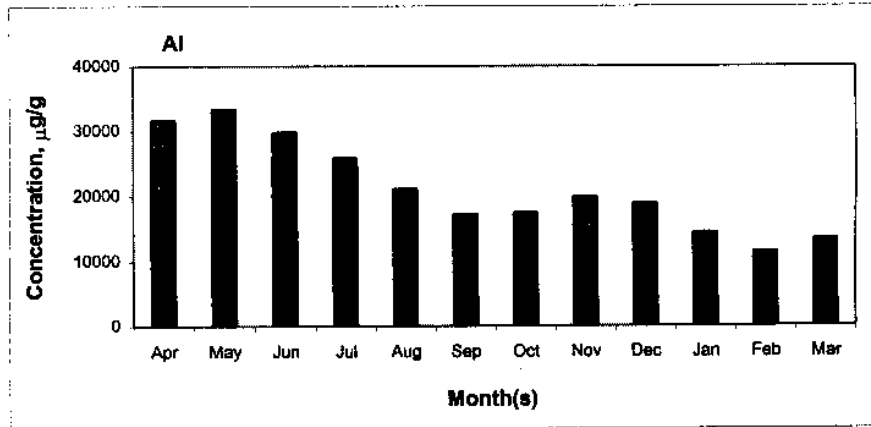
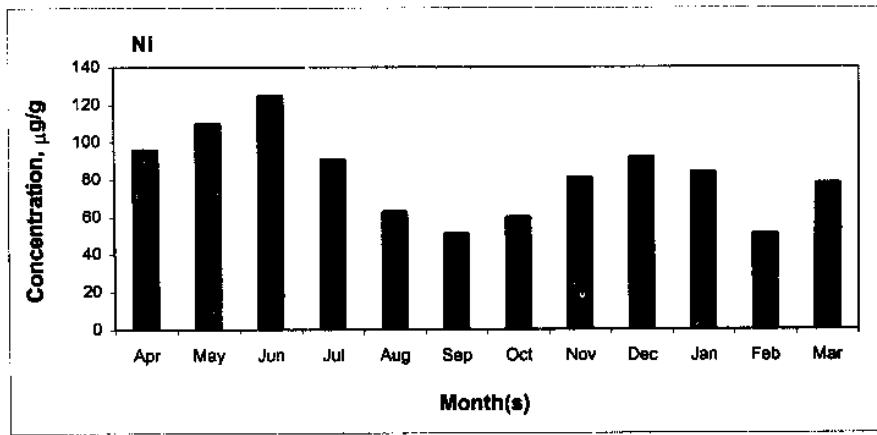


Fig. 5(c). Monthly variation of metal concentrations and organic matter in suspended sediments

Table 4. Correlation coefficients among metal concentrations in suspended sediments

	Flow	SS	Cu	Zn	Fe	Mn	Co	Cd	Cr	Pb	Ni	Al	OM
Flow	1.000												
SS	0.179	1.000											
Cu	-0.452	-0.218	1.000										
Zn	-0.649	-0.302	0.844	1.000									
Fe	-0.648	-0.125	0.895	0.773	1.000								
Mn	-0.621	-0.070	0.697	0.807	0.662	1.000							
Co	-0.496	-0.200	0.918	0.787	0.843	0.827	1.000						
Cd	-0.635	0.359	0.551	0.563	0.716	0.748	0.597	1.000					
Cr	-0.478	-0.315	0.881	0.840	0.718	0.781	0.930	0.432	1.000				
Pb	-0.658	-0.321	0.869	0.866	0.806	0.910	0.944	0.627	0.930	1.000			
Ni	-0.465	-0.566	0.675	0.574	0.743	0.321	0.613	0.163	0.614	0.605	1.000		
Al	-0.430	-0.128	0.940	0.762	0.903	0.717	0.966	0.588	0.861	0.856	0.669	1.000	
OM	-0.608	-0.442	0.886	0.793	0.901	0.714	0.909	0.519	0.851	0.914	0.808	0.896	1.000

sediments and the concentration of most of the heavy metals. Similar findings were also reported by Houba et al. (1983) for Vesdre river in eastern Belgium. A high positive correlation of most of the metal ions with iron, manganese and organic matter indicates that these constituents play a major role in transport of metal ions.

It has been clearly shown that the presence of heavy metals is affected by the particle composition of sediments (Yamagata and Shigematsu, 1970; Asami and Sampei, 1979; Thorne and Nickless, 1981). In sediments of polluted streams the largest amounts of heavy metals are associated with organic matter (humic and fulvic acids, colloids, synthetic organic substances), the fine-grained sediment fraction (clay, silt and fine sand) and Fe/Mn hydrous oxides, or are precipitated as hydroxides, sulphites or carbonates (Forstner, 1981).

Interactions between metals and organic matter in suspended sediment have often been recorded. Metal concentrations in the suspended sediments were positively correlated with organic matter content for all metals (Table 4). Correlation coefficients were high (>0.8) for Cu, Zn, Fe, Co, Cr, Pb, Ni and Al, and low for Cd. The high correlation coefficients of most of the heavy metals with organic matter further suggest the affinity of these metals for organic fractions of the sediments. Similar findings were also reported by Coquery and Welbourn (1995).

In natural waters there is a strong affinity between metals and organic matter (Forstner and Wittmann, 1981). Dissolved and particulate organic carbon in the water column act as scavengers for metals, and the scavenged metals may then be incorporated into the bottom sediments. In particular Hg and Pb are known to form strong complexes with humic substances. The highest correlation coefficient observed between organic matter and Pb also suggests the same possibilities of formation of strong complexes with organic matter in this study.

The relationship between organic matter and metal ion concentrations in suspended sediments are shown in Fig. 6 and regression equations explaining the variation of metal concentration in suspended sediments with organic matter are given in Table 5 along with respective coefficient of determination (r^2). As is evident from the values of coefficient of determination, the

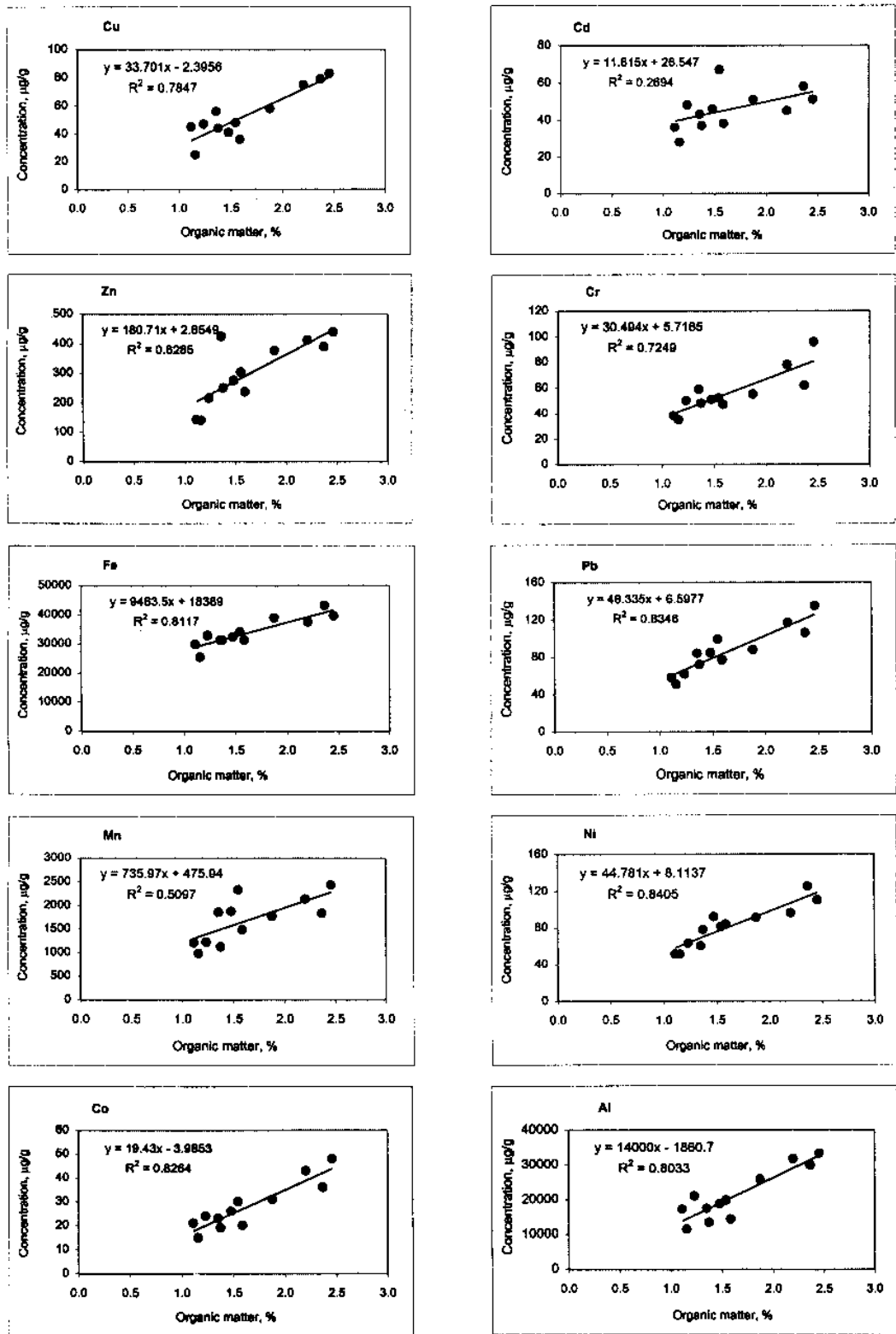


Fig. 6. Relationship between metal concentrations in suspended sediments and organic matter

Table 5. Regression equations for different metals in suspended sediments

Metal	Regression equation	Coefficient of determination
Cu	$y = 33.701 x - 2.3956$	0.79
Zn	$y = 180.71 x + 2.8549$	0.63
Fe	$y = 9463.5 x + 18389$	0.81
Mn	$y = 735.97 x + 475.94$	0.51
Co	$y = 19.43 x - 3.9853$	0.83
Cd	$y = 11.615 x + 26.547$	0.27
Cr	$y = 30.494 x + 5.7165$	0.73
Pb	$y = 48.335 x + 6.5977$	0.83
Ni	$y = 44.781 x + 8.1137$	0.84
Al	$y = 14000 x - 1860.7$	0.80

y = Metal concentration; x = Organic matter

relationship is well defined for all the metals except Mn and Cd.

4.3 Heavy Metal Concentrations in Bed Sediments

The monthly variation of heavy metal concentrations in bed sediments (0-200 μm) of river Hindon is shown in Fig. 7. Metal concentrations are generally lower in bed sediments than in suspended sediments. This could be attributed to the prevention of sedimentation process by water currents. This again indicates the importance of suspended sediments in the transport of heavy metal ions.

The highest concentrations of metal ions were observed in summer season. The concentration of metals decreased in the bed sediments during the monsoon season. During monsoon season, polluted particles (especially fine fraction) is supposed to disperse through suspension in the bottom sediment layer, and thus their distribution in the surface sediment was expected to become similar to effluent dilution or dispersion in the water of the river. Similar findings were also reported by Geesey et al. (1984). Following peak discharge, the presence of the metals in bed sediments increased as the flow again decreased. The highest accumulation of metals occurs in low flow period and the lowest accumulation of metals occurs during the high flow period, suggesting that the distribution of heavy metals in bed sediments is brought about by changes of the water flow. Therefore, sediment analysis should be carried out in low flow conditions, where highest accumulation of metal takes place from water to sediments.

The correlation coefficients among various heavy metals are shown in Table 6. A fairly good correlation of Mn, Co, Cr, Ni with Fe and Co, Cd, Cr, Pb, Ni, and Al with organic matter was observed. However, the correlation coefficients are significantly lower than the ones observed in suspended sediments. This is due to the fact that most pollutants are generally concentrated in the fine particle fraction of the sediments due to large surface area.

The relationship between organic matter and metal ion concentrations in bed

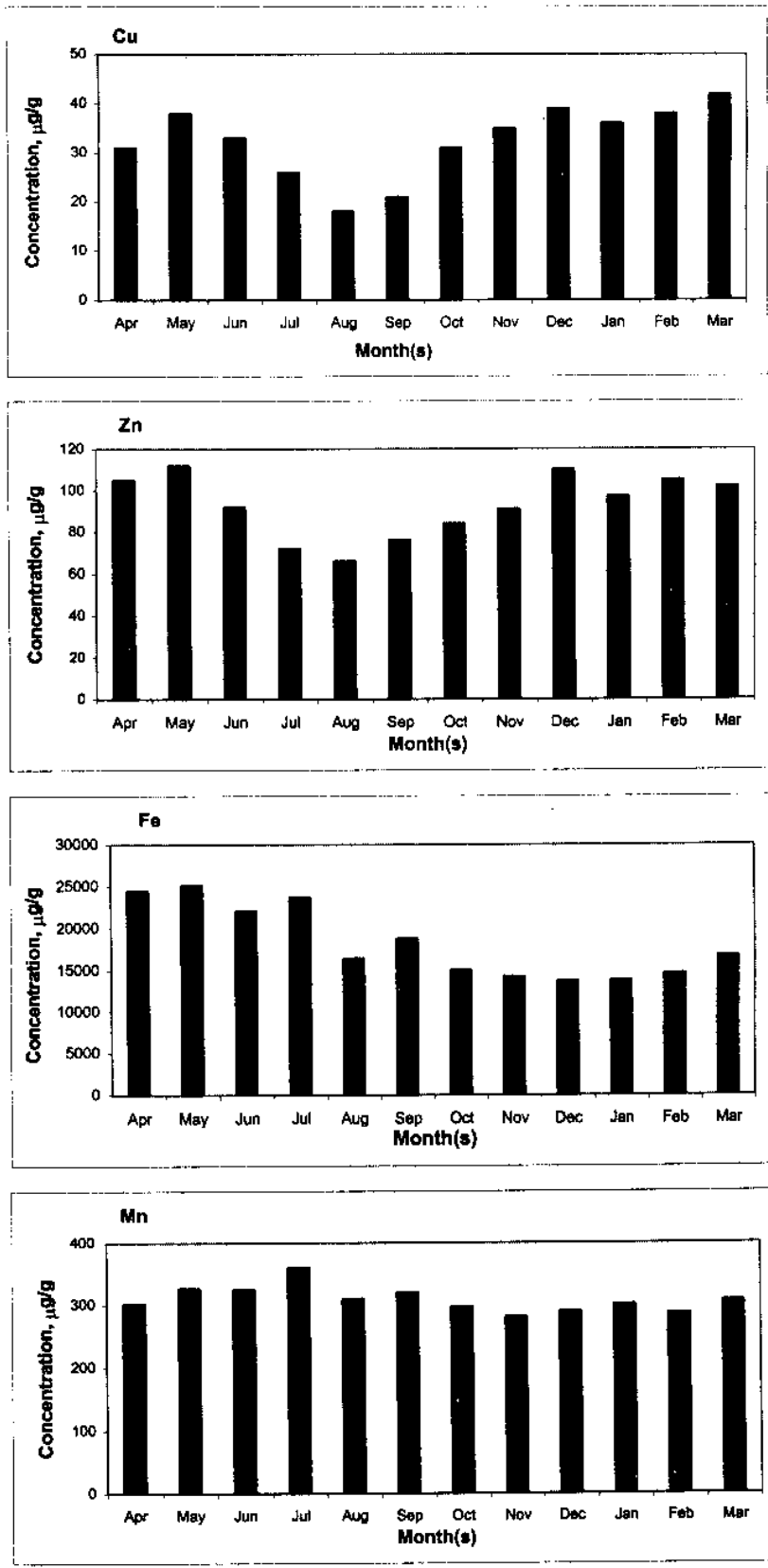


Fig. 7(a). Monthly variation of metal concentrations in bed sediments

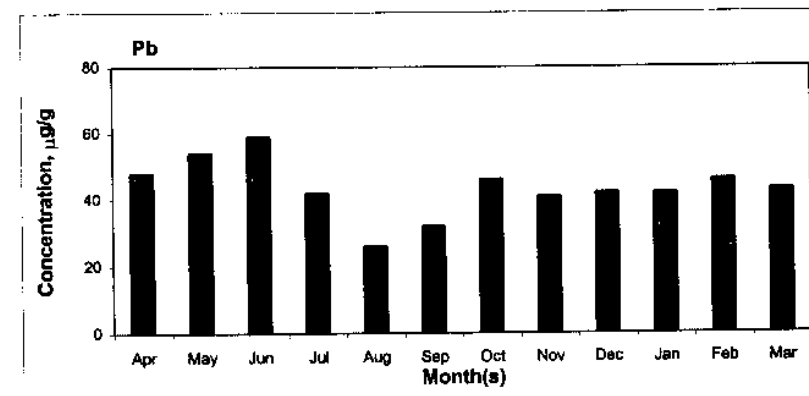
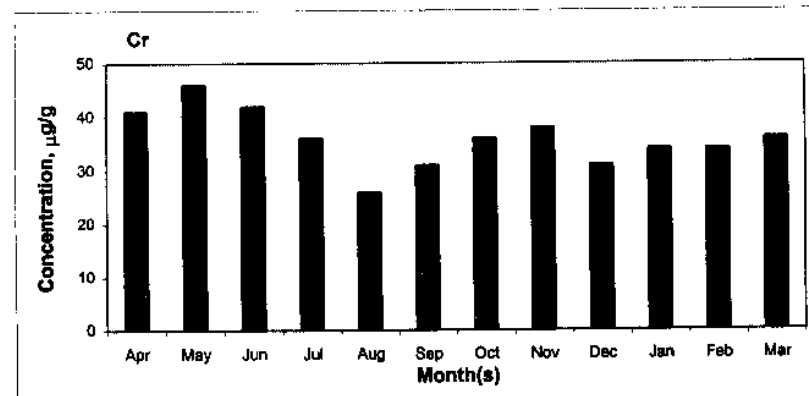
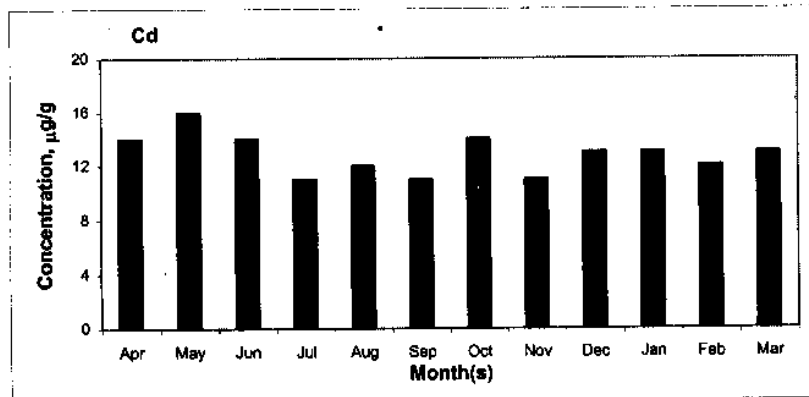
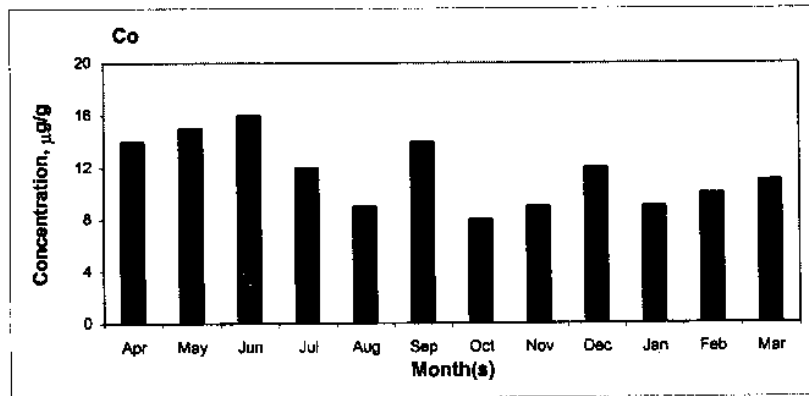


Fig. 7(b). Monthly variation of metal concentrations in bed sediments

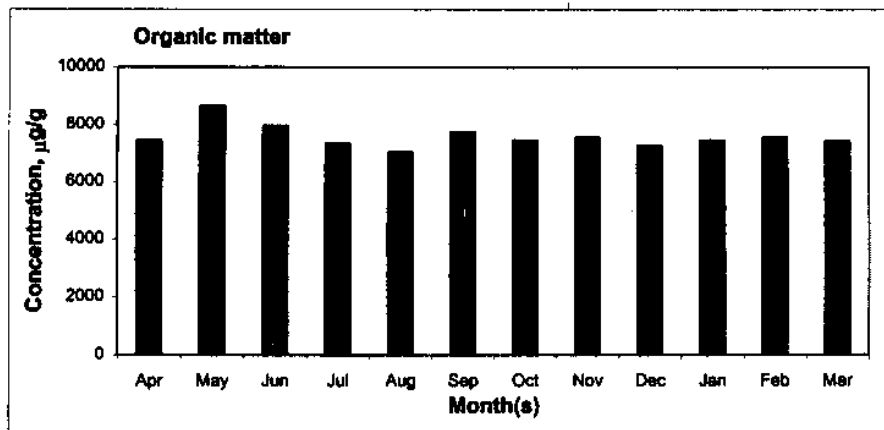
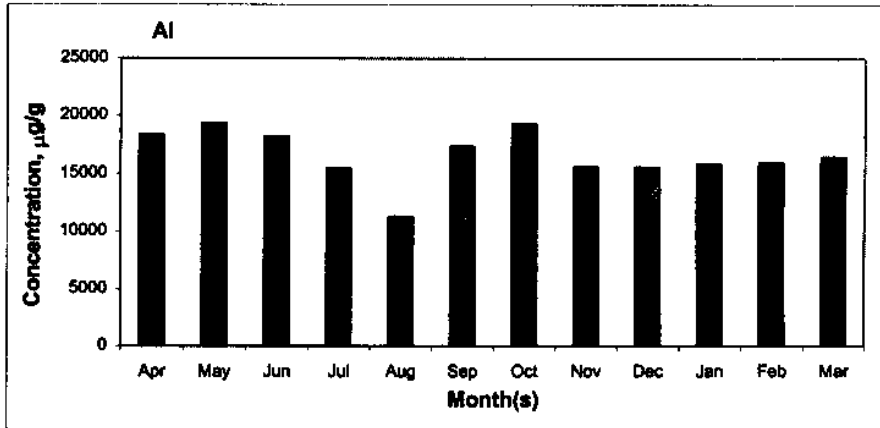
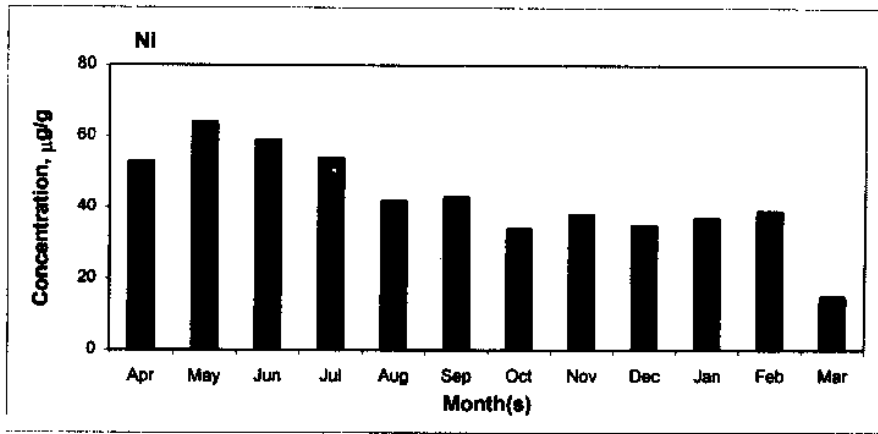


Fig. 7(c). Monthly variation of metal concentrations and organic matter in bed sediments

Table 6. Correlation coefficients among metal concentrations in bed sediments

	Flow	Cu	Zn	Fe	Mn	Co	Cd	Cr	Pb	Ni	Al	OM
Flow	1.000											
Cu	-0.338	1.000										
Zn	-0.211	0.808	1.000									
Fe	-0.259	-0.293	0.018	1.000								
Mn	-0.191	-0.474	-0.416	0.733	1.000							
Co	-0.096	-0.129	0.265	0.779	0.503	1.000						
Cd	-0.311	0.497	0.677	0.484	0.072	0.552	1.000					
Cr	-0.494	0.299	0.523	0.641	0.210	0.549	0.657	1.000				
Pb	-0.394	0.454	0.623	0.435	0.100	0.503	0.660	0.873	1.000			
Ni	-0.313	0.078	0.125	0.937	0.696	0.808	0.611	0.707	0.543	1.000		
Al	-0.121	0.107	0.469	0.423	0.079	0.477	0.481	0.770	0.749	0.374	1.000	
OM	-0.043	0.166	0.419	0.525	0.254	0.624	0.637	0.765	0.633	0.661	0.674	1.000

sediments are shown in Fig. 8 and regression equations explaining the variation of metal concentration in bed sediments with organic matter are given in Table 7 alongwith respective coefficient of determination (r^2). As is evident from the values of coefficient of determination, the relationship is not well defined for most of the metals.

Similar studies of the presence of heavy metals in sediments have been widely carried out, but each sediment sample generally makes an inhomogeneous composition, depending on the geological characteristics of a particular area. Most pollutants may generally be assumed to be concentrated in the fine particle fraction of the sediments (Yamagata and Shigematsu, 1970; Mizobuchi et al., 1975; Asami and Sampei, 1979; Thomson et al., 1984). The different distribution of particle size may give different heavy metal concentration in the same sediment sample. The concentration of metal ions in different fractions of uncontaminated sediments also shows significant difference indicating how natural (background) metal concentrations increases in proportion to the percentage of fine material (Duzzin et al., 1988). Yamagata and Shigematsu (1970) have also pointed out that heavy metals should not be analysed simply in the total sediment, but that it should be carried out with due consideration of the particle size itself. Particular attention has been paid in published work to relatively small particles that pass through a sieve aperture of 125 μ m (Forstner and Wittmann, 1981), with ratio of surface area to volume an important factor (Forstner, 1983).

The distribution of heavy metals in different fractions of the bed sediments of river Hindon for pre-monsoon (June 1999) and post-monsoon (October 1999) seasons has been studied and is shown in Fig. 9. Lower metal concentrations in bed sediments during post-monsoon season established that monsoon had a slight effect on status of metals in sediments by causing renewal and mobilization of metals from the sediments. Considering that in the post-monsoon season, contaminants might have been mobilized by the preceding floods, it seems advisable to sample when the low water regime is stabilized.

The differences in the weight percentages of sediment fractions, organic carbon and in the composition of the various fractions during the two surveys are related to the hydrologic event (monsoon) which occurred in between the two surveys. The decrease in the fine sediment fractions,

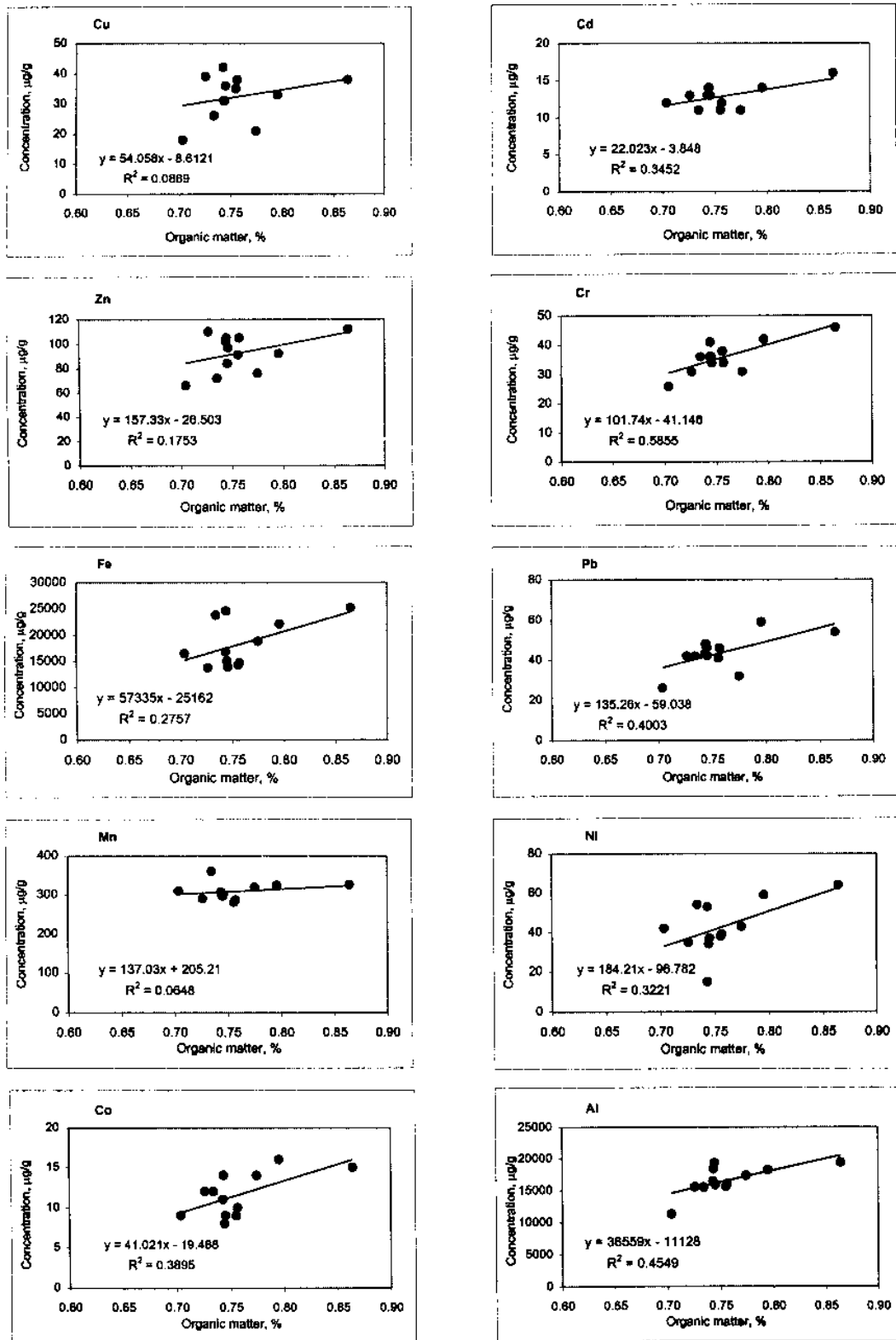


Fig. 8. Relationship between metal concentrations in bed sediments and organic matter

Table 7. Regression equations for different metals in bed sediments

Metal	Regression equation	Coefficient of determination
Cu	$y = 54.058 x - 8.6121$	0.09
Zn	$y = 157.33 x - 26.503$	0.18
Fe	$y = 57335 x - 25121$	0.28
Mn	$y = 137.03 x + 205.21$	0.07
Co	$y = 41.021 x - 19.488$	0.39
Cd	$y = 22.023 x - 3.848$	0.35
Cr	$y = 101.74 x - 41.146$	0.59
Pb	$y = 135.26 x - 59.038$	0.40
Ni	$y = 184.21 x - 96.782$	0.32
Al	$y = 36559 x - 11128$	0.46

y = Metal concentration; x = Organic matter

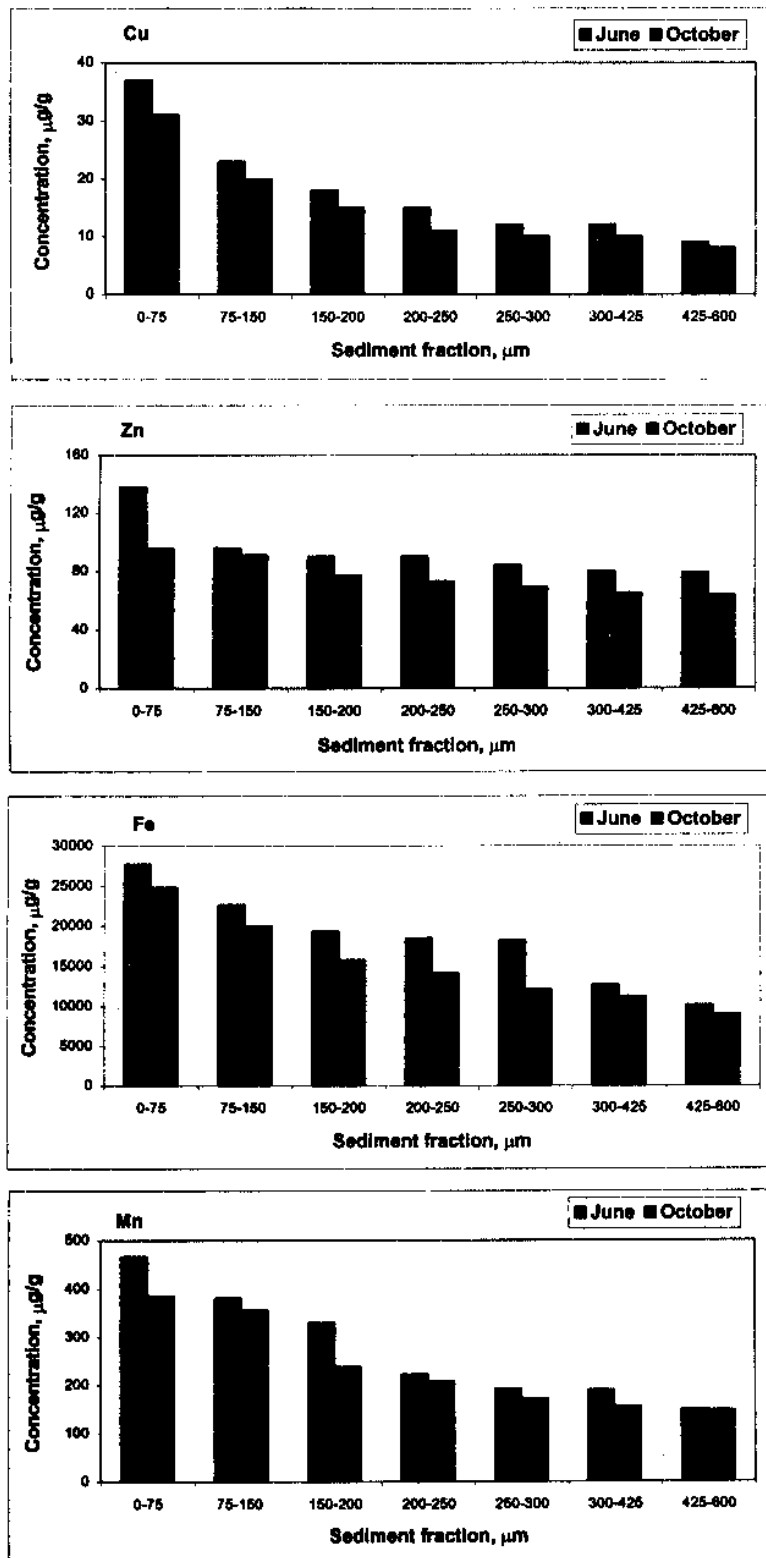


Fig. 9(a). Distribution of metal concentrations in different fractions of bed sediments

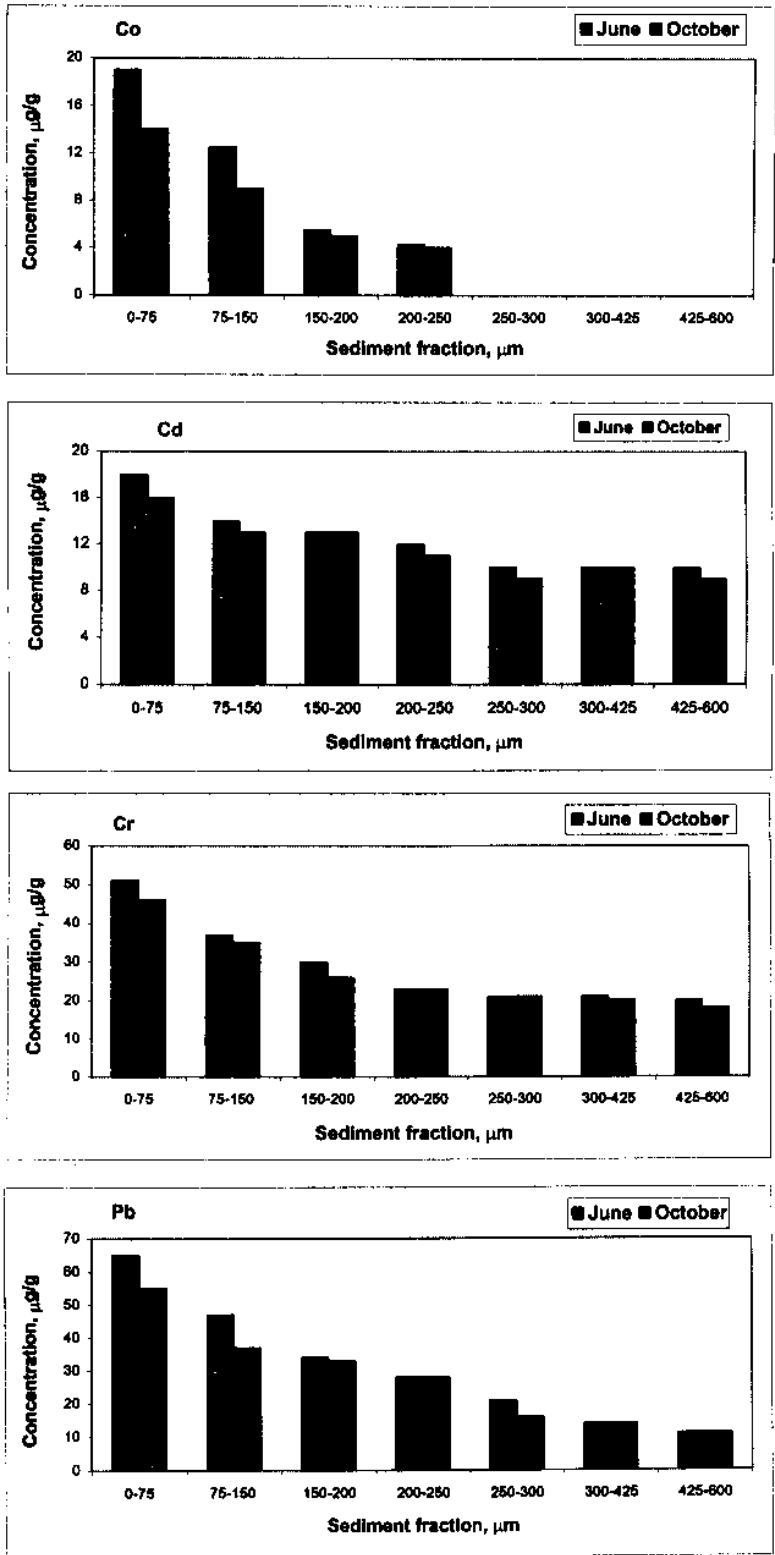


Fig. 9(b). Distribution of metal concentrations in different fractions of bed sediments

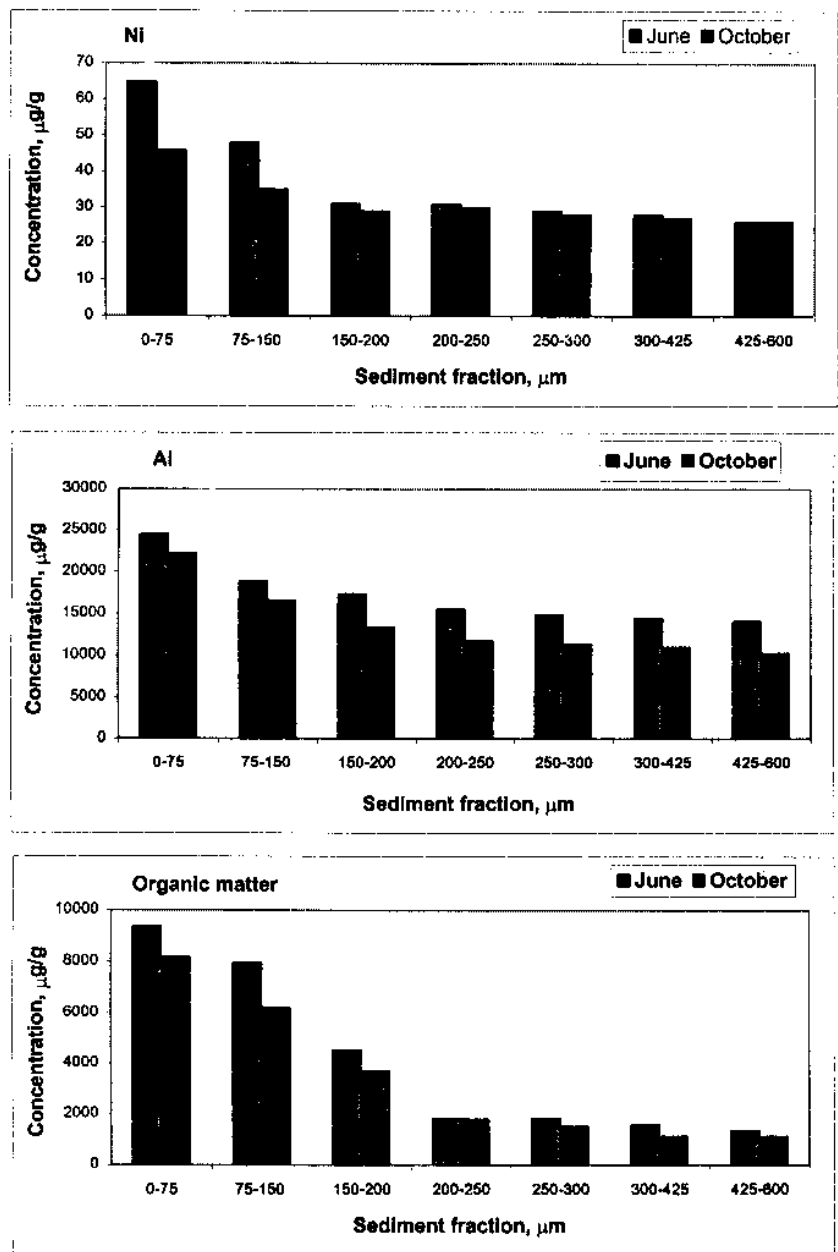


Fig. 9(c). Distribution of metal concentrations and organic matter in different fractions of bed sediments

organic matter and concentration of metal ions in fine fraction (0-75 μm) during post-monsoon season indicates that large amount of particulate matter is transported to the river as a consequence of high precipitation during monsoon season. Excess flow washes away the more contaminated superficial sediments, which settle in the low flow conditions during summer, substituting them with other less contaminated sediments from the basin.

It is clearly evident from the results that the concentration of different metals is dramatically different in different fractions of the sediments. The heavy metal concentration generally increased with the decreasing particle size of the sediments. It appears clear that the pollutants accumulated according to the fraction size $0-75 > 75-150 > 150-200 > 200-250 > 250-300 > 300-425 > 425-600 \mu\text{m}$. The concentration of each metal decreases from fraction 0-75 to 425-600 μm step by step. The general trend is an increase in the presence of heavy metals with decreasing particle size. The fraction 0-75 μm , therefore, has the highest concentrations. This fraction of the sediment is very important because it is considered to be the potential mobile fraction of the sediment under the normal conditions of the river system.

5.0 CONCLUSION

It is evident from the study that the concentration of heavy metals in water is highly influenced by the flow of the water. Sediment analysis provides a much stable base for monitoring the pollution of an aquatic environment by heavy metals, which are easily accumulated in suspended and bed sediments. The content of fine fraction, organic matter and Fe/Mn plays an important role in the transport of metal ions and helped in interpreting sediment data. The sediment analysis should be carried out in low flow conditions because heavy metal pollution may be highest during this period and it may be accumulated from water to sediments. Numerous studies have also demonstrated that the determination of metal concentrations in suspended and bed sediments is more sensitive than dissolved concentrations as indicators of contamination in hydrologic systems.

There is an urgent need for more critical identification of environmental problems of metal contamination in other basins also. The study shows that indiscriminate discharge of untreated waste water and industrial effluents from over crowded residential and industrial areas can pollute urban river systems. Under conditions of high water discharge (monsoon period) erosion of riverbed takes place in local river systems. However, within the dry periods of reduced rate of flow, a fraction of suspended sediments in polluted stream water is partially incorporated into the bottom sediment in many sections of the river systems. On such sites a sampling scheme based on the collection of representative samples of stream bottom sediments, stream water and waste water may be effective in source assessments. Further studies are also needed on metal speciation and effects on metal uptake by organisms. The effective exposure of organisms to different metals is influenced by both changes in metal speciation and relative distribution of metals between particles of different sizes and densities.

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