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Techniques and technologies available for quantification of heavy metals found in water and sediment

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Abstract

Sediment serves as a reservoir for heavy metals and therefore, deserves special consideration in the planning and design of aquatic pollution research studies. An undisturbed sediment column contains a historical record of geo chemical characteristics. It will allow an investigator to evaluate geo chemical changes over time, and possibly, to establish baseline levels against which current conditions can be compared and contrasted. Metals may be mobilized as a result of natural processes (e.g., weathering and erosion of geo chemical formations) as well as by anthropogenic activity. In the mobilization process, trace elements may be absorbed by days, can complex with organic compounds or may co-precipitate with oxide and hydroxides. Indeed sediment shows a high capacity to accumulate and integrate on time.

Keywords: Heavy metals, aquatic pollution, water and sediment.

Introduction

Estimation of heavy metals particularly in natural aquatic system played a very important role in environmental monitoring process, since geological and anthropogenic inputs dominates the carrier compartment of the water column of a river system, hence the river water and sediment of world are bound to vary in their effect on heavy metal distribution The biological availability of heavy metals in sediments is governed by numerous factors including precipitation, adsorption onto the organic and inorganic sediment fractions

Heavy metal analysis

Heavy metals gain access in river system from nature as well as from anthropogenic sources and get distributed in water, suspended sediments and sediments during the course of their transport (Allen, R.J., 1979). In Yamuna river high values of Cd (iv), Ni has been reported at Mathura and Agra (Kudesia, V.P.). The horizontal distribution of heavy metals in the top layers of the sedimentary column has been proved to be useful in tracing sources and dispersal patterns of metal pollutants in aquatic environments. Concentrations of Hg, Pb, Ni, Co, Zn, Cr and Fe in surface sediments sampled in the lagoon of Venice were processed using two mathematical, statistical methods. Principal component analysis and cluster analysis were combined in order to assess the degree of contamination in different areas of the lagoon to determine the sources and to trace the diffusion paths. Data was normalized to the natural concentration of metals determines, from the deepest section of sediment cores (Pavoni, et. al., 1988). The heavy metals like Pb, Cd, Cu, Ni, Co, as well as other chemical parameters of the sediment have been analyzed by multivariate statistical method in order to explain the behaviour of the heavy metal in the zone.

The low concentration of trace elements in water allow the determination of metals even when levels in water are extremely low and undetectable with current methods of analysis. The enrichment rate of pollutants in river sediments reflects the upstream contamination sources. Distribution of heavy metals like Mn, Cu, Fe, Cr, Cd and Zn in water and sieved samples in Toyohira River polluted by municipal, industrial and mining effluents, which flow through the city of Sapparo, were studied (Sakai, H., et al. 1986). The concentration of seven heavy metals viz., Fe, Co, Mg, Cu, Ni, Cd and Zn in water and bed sediments of river Ganga have been studied for the 480 km. stretch from Badrinath to Narrora (Saikai et al., 1988). Dhanmondi and Rama lakes, situated at the heart of the Dhaka city, have been receiving industrial as well as domestic sewage, analysis of a number of a sediment samples collected from the bed and the lakes showed that it is contaminated with Cu, along with other heavy metals (Baderuzzaman et al., 1999). Copper, the most common among the heavy metal, is toxic to aquatic lives, in trace amounts, if present in the water system and sediment of lakes. The sediments of Ramganga River, Moradabad which receives industrial effluents from brass factories, stainless steel, electroplating units etc, besides partially treated and untreated sewage is rich in heavy metals like Cu, Pb, Ni, Cd, Fe and Zn (Pande, et al., 1999).

The mechanism of heavy metals adsorption and adsorption capacity of the sediment (Biswal, et al., 2000) have applied the Freundlich isotherm to data relating to heavy metals adsorption to river sediments. The studies on the Gomati river sediment show relatively higher values of Cu, Mn, Pb, and Cr in comparison to background values (Kumar, 1989). It is reported that the municipal waste discharged in to the river through drains are responsible for the higher values of heavy metals in the sediment of the river. Srivastava et al., 1988, reported that the Ganga river is under the stress of urbanization, industrialization. The five dyes based metallic elements namely Mn, Cu, Fe, Cd, Hg and Zn were recorded in the river water and sediments above the permissible levels. It is known from literature that anthropogenic influences contribute much in metal contamination in river. Kumar, D., 1986, studied that the heavy metals content in the sediment of Narvada gedda stream, Visakhapattnum and observed that the levels of Mn, Cu, Fe, Cr, Cd, Hg and Zn were alarmingly high. Extensive studies were carried out on water, sediments, plants and fish of Kalindi (U.P.) to find out the accumulation levels of heavy metals (Mn, Cu, Fe, Cr, Cd and Zn). Nair and Balchand (1993) studied the speciation of trace metals in sediment of a tropical estuary. Metals like Mn, Cu, Fe, Cr, Co, Cd, Hg and Zn were partitioned into the filterable, adsorbed and ion exchangeable fractions. The Hussain Sagar Lake in Hyderabad is highly polluted by the industries situated around it. The distribution for heavy metals namely Pb, Cu, Fe, Cr, Cd, Hg and Zn in the surface sediments were also investigated for the presence of Pb, Cu, Ni, Cd, Hg and Zn to find out whether their was seepage of these metals in to the ground water (Srikant, et al., 1993). The ground water samples collected within the radius of 1km. showed consistently higher concentration of these metals. Padamlal and Seralathan, 1993, studied the heavy metal concentrations in the suspended particles and bed sediments of a tropical perennial river and estuary in Kerala, results indicated that concentration of Ni, Cu and Zn were enriched in the particulates phase. The concentration of Pb, Cd, Zn, Cr, and Mn in surface sediments collected from the Antartic marine ecosystem (Andrade, S., et al., 2001) was measured by AAS. The determination of toxic metal concentration allows the evaluation of the seawater quality, especially if such metals are determined in suspended particles and their subsequent transfer to sediment has been reported (Frostner, 1989). Metals like of Hg, Pb, Cd, Zn, Cr, and Cu are strongly associated with bed sediments and for this reason the determination of elemental concentration at different depths of a sediment column gives information regarding temporal pollution trends and consequently the contamination history of the considered aquatic ecosystem.

Instrumentation methods

To carry out such study, sensitive and accurate instrumental analytical techniques are required. For trace metal determination, several techniques can be employed (Clement, et al., 1995). Anodic voltammetry, atomic absorption spectroscopy with inductively coupled plasma excitation, neutron activation analysis and x-ray fluorescence are more frequently used. The choice of most suitable analytical technique for the determination of metals at ultra trace levels must consider several parameters, such as sensitivity, selectivity, detection limit, sample preparation, analysis time and instrumental cost. Differential pulse anodic voltammetry (DPASV) is one of the best owing to its ability to simultaneously determine several elements at ultra trace levels (Locatelli, et. al., 1996) and its low cost. Voltammetric techniques have the added advantage of identifying the oxidation state of the element (speciation) and of carrying out automatic on line monitoring measurements (Acterberg and Vanderberg, 1994). However, the main limitation of the anodic stripping voltammetry in comparison with the spectroscopic techniques is the limited number of the elements that can be determined because they must form an amalgam (Wang, 1985). The analytical determination of heavy metals in the sediment and in water, sampled in the Yamuna river by employing differential pulse anodic voltammetry (DPASV) and graphite furnace atomic absorption spectroscopy (GFAAS) was carried out by Locatelli, et al, 1999 and a comparison was made by evaluating the analytical parameters of merit e.g. precision, accuracy, sensitivity and detection limit. Mercury determination was carried out by cold vapour atomic absorption spectroscopy (CVAAS). A reconnaissance survey of the extent of metal contamination in the Rio Grande de Tarcolesn river system of Costa Rica indicated high levels of Cr in the fine grain bed sediments of tributaries downstream from leather tanneries. In the main channel of the San

Jase urban area, chromium contamination in sediments was 4-6 times background and remained relatively constant over 50km to the mouth of the river. Sediments from a mangrove swamp at the river mouth had chromium level 2-3 times above background (Fuller, et at, 1990). The concentration of heavy metals in the fine fraction (<63 mm) of a surficial sediment samples from the border region of Baja California (Mexico) and California (USA) were Cu (4.9-2.3); Ni (16-44); Cr (56-8002); Pb (6-21); Cd (0.08-0.64); Ag (0.01-0.28) and Mn (92-1506), the interval for Fe and Al were 1.36-4.6 and 3.61-8.55, respectively (Villaescusa-celaya et.al, 2000) The concentration of heavy metals viz, Fe, Cu, Ni, Cd and Zn were determined in river sediments collected at the Ave river basin (Portugal) to obtain general classification scenery of the pollution in this highly polluted region (Soares et al., 1999).

Rios-Arena et al, 2003, in Rio Grande, carried out an assessment of heavy metal concentration in water and sediment. They determined heavy metal concentration and physico-chemical characteristics in water and sediments samples. Heavy metal analysis was done by ICP (Inductively Coupled Plasma Emission Spectroscopy). Oryari and Wandiga, 1989, reported many metals in the sediment of lake Victoria, East Africa and found a positive correlations between copper and zinc; manganese and iron; copper and cadmium; and copper and lead. Rao, et al., 2001 observed many heavy metals in the Kolleru lake, India which resulted that the sediments of Kolleru lake were highly contaminated by heavy metals, which are responsible for degrading the water quality of lake. They analyzed their samples by AAS (Atomic absorption spectrometer) and by ICP-MS (Inductively coupled plasma mass spectrometer).

Kaushik, et al., 2001, investigated heavy metal pollution in river Yamuna, at Haryana, with respect to possible impacts on human health and aquatic life. There is a negative correlation between Zn-Cd and Ni-Cd, while positive correlation between Zn-Ni. Fe, Ni and Co concentration exceeds the maximum permissible limits prescribed for drinking water all along the river and start accumulating these metals in human body tissues, which affect their body metabolism. Mahamed, et al., 1998, studied lead and cadmium in Nile river water and drinking water in greater Cairo, Egypt. The river water mean concentration were 29.4 $\pm$ 8.74 μg/l for lead and 4.15 $\pm$ 0.88 μg/l for cadmium. In the drinking water, the means were 9.93 $\pm$0.5 μg/l for lead and 63 $\pm$ 2.2μg/l for cadmium. Comparison of the raw and drinking water data showed that, the water treatment facilities reduced concentration of lead by 33% and cadmium by 53%. Singh, et al, 1993, studied water and sediment quality of rivers Damodar and Barakar in Bihar with respect to heavy metals distribution. The water of Damodar in this region gets an overdose of pollutants, which is beyond its capacity for self-purification, and concluded that most of the heavy metals were sorbed by sediment and coal dust particles available in river water. Chau et al, 1973 have also found high concentration of heavy metals in sediment than in water.

Israli, and Khursid, 1991, worked on distribution of heavy metals in Yamuna river water and sediments from Delhi to Allahabad. High concentration of heavy metals, i.e., Fe, Cu, Ni, Co, Pb, Cr and Cd in water were found. While in sediments content of these metals showed considerable variation at different sites, may be due to precipitation and sedimentation of these metals. Muller, et al, 1972, studied the heavy metal content in Ottawa River and Rideau River sediments and found that the source of metallic pollution was the municipal and industrial wastewater. A typical example of pollution caused by iron and steel industry has also been reported by Prater, 1975. It was found that iron and manganese had the highest mean concentration due to blast furnaces and ferromanganese plants. Coal fired power plant was found to be responsible for the elevation of metallic levels in water and sediments of upper Ganga Canal (Ajmal, et al., 1983). Agarwal, et al., 1978, conducted a survey of heavy metal contents in water and sediments and concluded that, Pb and Cu in the water and sediments are due to traffic of diesel and petrol vehicles. Dixit, et al., 2003, studied heavy metal contamination in surface and ground water supply of an urban city and found higher-level concentration of metal than prescribed by ISI. Das, et al., 2001,studied water sediment interaction in a fresh water system and concluded that the contamination of bed sediment of the river Brahamputra varies with depth as well as location. Considerable differences exist between the chemical composition of the pore water and the sediment. Yuan, et al, 2004 studied the speciation of heavy metals in marine sediments from the East China Sea by ICP-MS with sequential extraction. They found that more than 90% of the total concentration of V, Cr, Mo and Sn existed in the residual fraction. Fe, Co, Ni, Cu and Zn mainly (more than 60%) occurred in the residual fraction while Mn, Pb and Cd dominantly presented in non-residual fractions in the top sediments.

Granero and Domingo, 2002, monitored the levels of metals in soil of Alcala de thanoros, Spain and found the concentration of Be, Cd, Cr lower than the reference values, while the average As concentration (3.4 μg/g) was higher than the safety limit for risk cancer. Metal polluted soils constitute a major environmental problem. Consequently, they are subjected to detailed risk assessment and management studies (Prasad and Nazarath, 2000). Kishe and Machiwa, 2003, analyzed the distribution of heavy metals in sediments of Mwanza gulf of Lake Victoria, Tanzania. Sediment samples were studied for Cd, Cu, Cr, Pb, Hg and Zn by AAS. The highest concentrations (ppm) for Cu (26.1 $\pm$ 4.8) Hg (0.2 $\pm$ 0.05), Pb (30.7 $\pm$ 5.6) and Zn (45.4$\pm$ 13.1) were found at approximately 25 m from the shoreline.

A study was initiated by Liaghati, et al, 2003, to examine elevated metal concentrations and to assess horizontal and vertical distribution of those elements and concluded that the surficial estuarine sediments were only enriched in V. Overall, geo chemistry and mineralogy of the samples show the effect of both natural and anthropogenic inputs to the catchments, however natural processes are more dominant than anthropogenic inputs in concentrating metals. Muohi, et al., 2003 examined heavy metals in sediments from Makupa and Port-Reitz Creek systems, Kenyan coast. The sediment samples obtained were digested using concentrated HCl and analysed by AAS (Atomic Absorption Spectrometer) and Energy Dispersive X-ray fluorescence techniques. There was significant (P = 0.05) variation in the elemental concentration between and within sites. Industrial activities and a nearby municipal dumpsite were associated with the higher elemental concentrations.

Pereira, et al., 1998, investigated that the accumulation of toxic and persistent substances in the coastal environment continuously increases owing to anthropogenic activities and Calmano et al., 1993, reported that pH and redox conditions controlled the mobilization of Zn and Pb from contaminated sediments in a study from Hamburg harbor. Rees, et al, 1998, reported that large quantities of Pb and Zn, arising from mining related waste trapped in sediments with influvial system in the trent and ouse draining. The pennie orefield's, remained high between source areas and the Humber estuary, whereas Cr, which is associated with manufacturing industries, had high levels near source cities, but decreased rapidly down the river systems because of dilution by other sediments.

Fernadez et al., 1994, assessed heavy metal pollution in Jacarepagua basin, Rio de Janeiro and found that Pb in sediments outside areas of industrial region and close to motorways were high and originated from the combustion of leaded petrol. Further, Wci and Morisson, 1993, found that storm events led to significant changes in organic profile by resuspension/ deposition of cleaner background sediments and removal of organic rich sediments which were being washed downstream in a small urban river in Goteberg and reported that interstitial water during periods of dry and light rain combined with storm resuspension played a key role in metal diffusion and distribution in the river. Metal contaminants, which are stored in sediments, may have a greater influence on biological uptake than those in waters, particularly in the case of benthic faunas as reported by Breward et al., 1998.

Ramessur, et al, 2002, studied the concentration of lead, chromium and zinc in sediment of an urbanized river of Mauritius. The mean concentration of Cr and Zn are (105$\pm$ 30 mg kg^{-1}), (167 $\pm$ 30 mg kg^{-1}) respectively in the sediments along St. Louis river. Odiel river estuary is one of the most industrialized areas in Southern Spain and consequently, receives, the discharge of industrial and urban waste. Morillo, et al., 2002, studied the chemical partitioning of metals (Cu, Zn, Cd, Pb, Fe, Ni, Cr and Co in four fraction (acid-soluble, reducible, oxidizable and residual) of Odiel River and showed that, Cd had the highest percentage in the acid-soluble fraction (the most labile) and the lowest in the residual fraction. However, Pb, Fe, Cr and Ni, were present in the greatest percentage in the residual fraction, which implies that these metasl are strongly linked to the sediments.

Sediments are the main sinks for the heavy metals, but when environmental condition changes (pH, sediment redox potential, etc), Sediments can act as a source of metals (Zoumis, et al, 2001). Heavy metals are present in different chemical forms in sediments. It can be in the form of easily exchangeable ions, metal carbonates, oxides, sulfides, organometallic compounds, ions crystal lattices of minerals, etc, which determine their mobilization capacity and bioavailability (Weisz, et al., 2000; Yu, et al., 2001).

Pardo, et al, 1990, studied the determination and speciation of heavy metals in sediment of the Pisuerga River, i.e., Polluted by industrial and municipal waste. All heavy metals were determined by Voltammetric methods and their mean total contents were (in µg g^{-1}): Zn, 245.49; Cd 1.05; Pb 18.77; Cu 66.53; Ni 46.51 and Co 11.41. All the data were examined by Principal component analysis in order to explain the behavior of each metal on the sampling point. Sainz, et al., 2004, characterized heavy metal discharge into the Ria of Huelva, estuary, Spain. The obtained mean values showed two different types of heavy metal discharge in the estuary: during low water (50% of the days) with only 19.30 kg of heavy metals and during high water or flood (17% of the days), with 72.47 kg of heavy metal. Speciation was carried out by Tessier's method.

A considerably high metal level in water and sediments of the Yamuna river reported by Ajmal et al., 1985(b). Singh. M, 2001, also studied the concentration of 9 heavy metals in the Yamuna river sediment from Delhi to Agra. Chakravorty, et al., 1996, reported heavy metal concentration in different creeks of Hooghly Estuary along Calcutta Metropolis, during pre-monsoon and post-monsoon seasons. The seasonal pattern revealed that maximum amount coming out from the cracks was 0.719 ppm at pre-monsoon and 263 ppm at post monsoon. Sengupta et al., 1988, in their study on the pollution status of the Ganga river stretch extending from Berhampur to West Bengal, reported presence of some metal ions, such as Ti, La, Gd and Zr in large quantities.

. Baruah et al., 1996, studied heavy metal concentration in river Jhanji, Assam and showed a downward decreasing trend of heavy metal concentration. Jameel, 2000, examined the riverbed sediments for the distribution of organic matter and toxic heavy metal in the river Cauvery. He concluded that most of the heavy metals have precipitated and settled into the riverbed as carbonates, oxides, hydroxides and the pollutants are deposited in association with very fine particles of slit and clay. The slit and clay act as adsorbents along with the organic matter.

The deposition of heavy metals occurs in association with very fine particles of slit and clay. They decrease root-respiration and nutrient uptake by the plants. They inhibit cell mitosis in root meristamatic regions. Heavy metals reduce enzymatic activity and the microbial and micro faunal population in soils. They are environmentally stable, non- degradable and induce toxic effects. The heavy metals accumulate in the sediment due to adsorption process. The ability to absorb heavy metals is enhanced due to the presence of organic particles (Jackson, 1978). Dora and Ray, 1987, investigated water quality of Subernrekha river in the Bihar state. Kalita, et al., 1998, evaluated the water quality of Andaman and Nikobar Group islands and reported iron from 0.13 to 0.48 mg/L. Kakati and Bhattacharya 1990, studied trace metals in surface water of greater Guwahati and reported iron concentration fluctuated between 0.11 to 12.8 mg/l. Sivakuamar et al, 1990, reported iron between 0.2 and 2.5 mg/l in Bhavani River (R.N.). Sarver and Rafat, 1991, studied on Doodhganga River, Kashmir and found iron from 0.431 to 0.941. Garg et al, 1992, studied the trace metals trend analysis in river Ganga at Kanpur and reported Pb (0.047-0.168 mg/l), iron (0.008 - 0.189 mg/l); Cr (0.013- 0.226 mg/l); and Zn (0.005 - 0.178 mg/l) due to discharge of industries in downstream. Mathuthu, et al, 1993, studied quality of river Mukuvishi in Harare, Zimbabwe. Kataria, H.C, 1994, studied heavy metal contamination in Betwa River and found the concentration of different metals with in permissible limit. Chattopadhyay and Ray, 1990, studied sediment chemistry parameters in river Khanki and Swernarekha over a period of 10 months and found varying concentrations of different metals at different places which may be due to combination of natural and man made factors.

Singla, 2003, conducted laboratory column studies to investigate the sorption capacity and transport of Pb, Cr and Cd through agricultural soil and found that the agricultural soil exhibited a higher metal sorption capacity in comparison to the river sand. The order of mobility was Cr > Cd > Pb, and top layer of the soil retained most of the metals. Vevey, et al., 1993, determined the concentration and bioavailability of heavy metal in sediment in lake Yojoa (Honduras) and predicted the low bioavailability of heavy metals in sediments. Sediments in Marine system play a very important role in the environment. Paradip port is one of the east coast of India situated around 120 Km from Bhubanswar, Orissa. The heavy metals such as Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn had been investigated by Mohopatra, et al, 1996, to assess the extent of pollution. Satyanaryana et al., 1994 found that metal pollution in harbor and coastal sediments of Visakhapatnum and Tuticorin were due to untreated domestic sewage, industrial effluents and land runoff. Ramamurthy, et al., 2002, discussed the possible impacts on the environment due to the industrial effluents. The impact of water and soil pollution of Parvanaru river was estimated by determining the concentration of elements Cu, Zn, Mn, Cr, Cd, Pb, Ni, Al, Mg, by using ICP-AES (Inductively coupled plasma-atomic emission spectrometry). They found all the metals with in permissible limit. Tsai, Li-J, et al, 2002, assessed the influence of geo-chemical component in the sediments on remobilization of heavy metals into pore water and on distribution of heavy metal in geochemical phases. Average distribution coefficients and the ratio of heavy metal in pore water to total extractable heavy metal, were found in the decreasing order of Co, Zn, Cd, Ni, Pb, Cr and Cu.

Singh and Ansari et al, 1997, studied the sediment of the Gomati and Ganga rivers and their sediment. They were found heavily polluted with the metal from the anthropogenic activities. Winter et al, 2001, reported Fe concentration in flood plain lake sediment core, UK and found that the Fe concentration did not vary with sediment depth. Rao, et al, 2001, analyzed trace elements in sediment samples in and around Visakhapatnum. Trace elements analysis was performed by PIXE (Palette X-ray emission spectra) technique. They concluded that As, Pt, Zn and Pb were very high in the samples, and Fe was comparably lower than the standard value. Moreover the accumulation of metals from the overlying water to the sediment is dependant on a number of external environmental factors, such as pH, EC, ionic strength, anthropogenic input, the type of organic and inorganic ligands (Davies et al., 1991).

Manjappa and Puttaiah, 2004, quantified metal accumulation in the sediments of Bhadra River near Bhadravati town. The result revealed that heavy metals were practically uncontaminated and heavy metals in the riverbed sediments were well within the shale standards. Sahu et al., 1993, studied the trace metal content in drinking water resource and reported seasonal fluctuation in metal content. Kannan and Ramasamy, 1993 analyzed different metal ions such as Fe, Zn, Mn and Cu from water resource and concluded that metal contaminated water cannot be used for domestic purposes. A comprehensive monitoring survey was conducted by Woitke, et al, 2003, to assess the environmental pollution status of the river Danube. Besides other biological and chemical parameters, concentrations of Al, Cd, As, Cr, Cd, Fe, Pb, Mn, Hg, Ni and Zn were determined in sediments and suspended solids. An evaluation of the pollution status of the river was carried out by enrichment factors (EFs) calculated by using adapted background concentrations of heavy metals. Except single sampling sites and some tributaries, the pollution of the river Danube by metals can be regarded as rather low.

El-sammak and Kassim, 1999, reported heavy metal pollution in the sediments of Alexandria Region, Southeastern Mediterranean Egypt. Mahopatra, S.P., 1988, studied the distribution of heavy metals in polluted creek sediment, Bombay. He analyzed nine heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn). The average metal concentration in the sediment were 2.29, 37.25, 39.89, 103.38, 69825.0, 860.15, 105.08,54.08, and 169.60 μgg^{-1} for Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn respectively. Wassy and Jain, 1988, studied the heavy metal concentration in river Yamuna and it was found to be comparatively high. The concentrations of Mn, Ni, Cu and Co in zooplankton were studied by Subrahmanyan, 1990 and found that, the metals were considerably high in gelatinous organisms such as copepods and decapods than in mysides.

Govindan and Devika, 1991, inferred that the concentration of heavy metals leached from the sediment to the water column was inversely proportional to the pH of the water. Rajan et al, 1989, studied the heavy meal concentration in surface sediment of Vellar estuary. Regression analysis showed a significant negative correlation between metal concentrations and salinity as well as with temperature, where as a significant positive relationship occurred between metal concentration and organic content of the sediment. Morgan and Morgan, 1992 have investigated the bioaccumulation of lead, cadmium, zinc and copper in 5 species of earthworms obtained from an abandoned lead-zinc mine sites. Rai et al, 1990, have reported reduced biomass and nitrogenous activity due to increase in mercury and zinc, concentration in river Ganga. Kassim, et al., 1997, studied six heavy metals namely Cd, Pb, Ni, Zn, Mn and Cu at the upper region of the Euphrates River in Iraq and determined these metals seasonally in water, suspended particles, bottom sediments and aquatic plants. They found high concentration of metals in suspended particles while much lower concentration in bottom sediment. Mn has the highest concentration in sediment at all the season. Bel-Segarra, et al, 1997, studied surface sediments of the San Simon inlet of the Ria de Vigo in Galicia, north-west Spain. Sadiq and Zaidi, 1985, examined the metal concentration in the sediments of the Arabian Gulf coast of Saudi Arabia, and found very high concentration than the prescribed value. The vertical distribution of heavy metals in sediments from two rivers (Axios and Allakaman) in north Greece was reported by Samanidar, et al., 1991, and concluded that the anoxic condition prevailing of increasing depths due to the decomposition of organic matter, yield the migration of heavy metals of the upper parts of sediments column and the decrease of metal concentrations with depth in core can also be attributed to a heavy metals release as a result of early diagnosis and bioturbation effects as well.Stamoulies, et al, 1996 studied the geochemical phases of metals in Hudson river estuary. Sediments samples were analyzed for particle size and extracted metals were analyzed by inductively coupled plasma atomic emission spectrometer (ICP-AAS). Metals were found to be associated largely with the fine-particle-size fraction. Various metal/metal relationships exist among the phases and fractions were studied and highlighted by strong correlations such as Ni and Zn, Cu and Cd.

Yun, et al, 2000, studied the distribution of heavy metals (Cr, Cu, Zn, Pb, Cd, As) in roadside sediments of Seoul metropolitan city, Korea. They concluded that the roadside sediments were heavily polluted with heavy metals. Ahumada and Vargas, 2005, studied trace metal inputs, sedimentation and accumulation in San Vicente Bay, Chile and showed that the metals associated with particulate material from trap was Zn > Cr ≈ Cu ≥ Pb > Ni > Cd and the abundance of metals in sediments was Zn > Cr > Cu > Pb > Ni >Cd. Papadopoulos, et al., 1997, examined Cr, Cu, Fe, Ni, Pb and Zn in marine sediment and found the level of contamination very high. Bubb and Lester, 1993, indicated that the sources of metals and metalloids in the low land river system and assessed the magnitude of metal enrichment. Klavins, et al., 1995, determined the concentration and speciation forms of Pb, Cu, Ni, Cd, Zn and Mn in sediments from 49 lakes throughout Lativa. Regional variation in pollutant distributions of Pb, Cu and Cd concentration was due to anthropogenic load. The enrichment of metals in top layer of sediments is an estimate of the environmental pollution level. Another factor that determines metal concentrations in sediments is the, organic matter production and sedimentation in eutrophic water bodies.

Mohan, S.V., 1996, estimated the heavy metals in drinking water and developed a pollution index. The results indicated that the water was free from heavy metal pollution. The data monitored have been used to compute heavy metal pollution index (HPI) using weighted arithmetic mean method. Machiwa, J.F, 1992, reported heavy metal contents in coastal sediments off Dar Es Salaam, Tanzania and found Fe, Cr, Cd, Pb were higher in the sediments. Higher concentration of Pb and Fe was due to harbor activities. Vazquez, et al., 1998, examined dissolved metals in Alvarado Lagoon, Mexico, and found that the dissolved metal concentrations depend on the season. Cd concentrations were higher in a winter season and lower in a rainy season. The concentration of Cu and Pb were higher in the dry season with low values in rainy season. Cr and Fe concentrations were found higher in the rainy season and lowest in a dry season. The concentrations of Cd, Cu, Pb were found to be positively related to the salinity, and Fe and Cr did not change significantly with salinity. The distribution of metals (Cd, Cu, Cd, Cr, Fe, Ni, Pb, Mn and Zn) in bottom and suspended sediments from the ocean up to the Hudson river estuary were analyzed by Gibbs, R.J, 1994 and found that, bottom sediment metal concentration was maximum in harbor by 30 times for Cd, 20 times for Cu and 10 to 15 times for Co, Cr, Ni, Pb and Zn. Szefer, et al, 1996, studied heavy metal pollution in surficial sediments from the southern Baltic sea, Poland and showed that Co, Ni, Cd, Pb, Rb, Fe, Mg, Li and Al display an enrichment factor, EF_{Al}^{M} of about 1, indicating that these elements occur in the sediments dominantly anthropogenic in origin.

Jones, K.C, 1986, reported the distribution and partitioning of silver and other heavy metals in sediments associated with an acid mine drainage after discharge into the river Rheidol using a sequential discharged Cd remained easily or freely leachable and exchangeable. Non-lithogonic form of Ag and Cu were released from sediments by oxidation, while Cd and Zn were solublized predominantly by an acid-reduction extraction. The polluting contents of river sediments may show large variations caused by the nature and discontinuity of contaminant impacts. They may also be influenced by fluctuations in river flow and precipitation causing bed erosion, water drainage and run-off from the banks and catchment area. Floods may also cause contaminated materials to be transported from the tributaries to the river with variations in grain size composition, organic carbon content and sedimentation rate.

Lo and Fung, 1992, collected eight sediment cores from Hebe Haven studied for metals including Cd, Cr, Cu, Fe, Ni, Pb, Zn and Ca. ^{210}Pb and ^{137}Cs used to determine the time of deposition as well as the concentrations of these trace metal on the sediments and found that the concentration were very high. They are 0.930, 120, 131, 42.3 and 50.9 mg/kg for Cd, Cr, Zn, Cu and Pb, respectively. The corresponding enrichment factors were, 13(Cd), 7.0 (Cr), 2.9 (Zn), 5.2 (Cu) and 2.4 (Pb). The sedimentation rates calculated were in the range of 0.351-0.561 cm/y.

Saikai, et al., 1986, studied distribution of heavy metals in water and sieved sediments in the Toyohira River. They concluded that heavy metal concentrations generally increased with the decreasing particle size of the sediments. Seasonal changes in the concentration of particles of smaller size were greater than changes among the layer particles. A mechanical device for sediments resuspenion was used in Venice lagoon for sampling of surface sediment layer. Zinc and iron were determined in the sediment samples. Lower metal concentrations were detected in sediments with respect to resuspended particles (Calyo, et al., 1991). Suspended and bed sediments collected from the entire region of the Krishna river and its major tributaries were sampled by Ramesh, et al., 1990, and analyzed for heavy metals (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb) with the thin film energy dispersive X-ray fluorescence technique. There was considerable variation in the concentration of elements towards downstream, which may be due to the variation in the subbasin geology and various degrees of human impact. Suspended particles are enriched in heavy metals, throughout the basin relative to bed sediments. Total concentrations of Cu and Pb and the speciation of these metals in sediments of the river Tenes were studied by Rauret, G., 1988, in order to establish the extent to which they were polluted and their capacity of remobilization of the sediments and total Pb and Cu determined by AAS. Moriarty, and Hanson, 1988, studied heavy metals in sediments of the river Ecclesbourne, Derbyshire, and concluded that most of the metal upstream is associated with mineral grains and in downstream most of the metal is retained.

Grimshaw, et al., 1976, found metal levels in solution are highest at low flow, suggesting absence of dilution effect. Madhystha, et al., 1996 studied heavy metals in Neteravathi river and found the concentration of all metals were below the permissible limit. Nair, et al., 1991 studied heavy metal speciation in sediments of Cochin estuary by using chemical extraction techniques. The forms determined were exchangeable cations, carbonate bound, easily reducible (combined with Fe-Mn oxides), organic/ sulphide phases and residual fractions. The concentrations determined indicated selective accumulation of the various metals in the different phases of the sediments, with spatial variability. Green-Raiz and Osuna, 2003, reported heavy metal distribution in surface sediments from a subtropical coastal lagoon system. They found a higher concentration of heavy metals in sediments.

Singh et al., 1996, studied the concentration of trace metals namely Zn, Pb, Mn, Cd, Sb, Cu, Co, Fe, and Ni in the water of river Beas. They collected samples from Manali to Pongdam and found that the concentration of heavy metals, (Mn and Fe) were fairly exceeded permissible limits of drinking water. Wang, et al., 2003, studied atmospheric deposition of heavy metals in the Pearl River delta (PRD), China. The samples were analyzed for heavy metal concentrations and Pb isotopic compositions. According to the analytical results, atmospheric deposition of metals (Cr 6.43 $\pm$ 3.19; Cu 18.6 $\pm$ 7.88, Pb12.7 $\pm$ 6.72; and Zn104 $\pm$ 36.4 mg/m^2/yr), in the PRD was significantly elevated compared with other regions, e.g. the Great Europe. It was also found that atmospheric deposition of Cu, Cr and Zn, was generally higher in the summer that than in the winter, which, could be caused by the wash out effect of the rainy seasons in the subtropical region. Isotopic composition of Pb in the air deposits (^{206}Pb/ ^{207}Pb 1.161-1.177) indicated that atmospheric inputs of Pb derived mainly from anthropogenic sources, e.g. vehicular exhaust. Wisseman and Cook, 1997, reported heavy metal accumulation in the sediments of a Washington lake and found Pb in the highest concentration followed by Mn, Cu, Zn, Ni, Cr, Cd and Co.

Heavy metal contents (Cd, Co, Cu, Mn, Pb, Zn) were studied in bottom sediments of the Dniper reservoirs and found that the concentrations of heavy metals were high in the sediment (Nakhshina and Belokan. 1991). A study on heavy metal pollution in the Chao Phraya river estuary indicated that the accumulation of Cd, Cr, Pb, and Cu in the river mouth vicinity was significant, which may have a long-term impact on the aquatic environment through precipitation of heavy metals to the bottom sediments. The heavy metal content detected higher in river than the prescribed value (Polprasert, C., 1982).

Shine, et al, 1995, examined 13 sediments cores for 10 metals and organic carbon along a pollution gradient from highly contaminated sediments in New Bedford Buzzards Bay. Lietz and Galling, 1989, studied concentration of heavy metals (Zn, Cd, and Pb), which is bound to the sediment of river Oker, in the federal republic of Germany, by using dialysis pipes for separating sediments with the medium and medium contain 1 μm EDTA for desorption. The concentration of heavy metals was found very high. Desorption only occurred in a maximum up to 2% of the total concentration. Prohic, et al., 1989, examined the factors that govern heavy metal concentration in sediments by a combined analytical, geo chemical and geological approach. Fytianos, and Louranton, 2004, worked on speciation of elements at Volvi and Karonia lake sediment of North Greece and concluded that Cd, Pb, Ca and Cr are associated with the oxidizable, carbonates and residual fraction. Zn and Fe associated with residual and reducible fractions. Banat and Hawari, 2003, examined the pollution load of Pb, Zn and Cd and mineralogy of the recent sediments of Jordan river/ Jordan and observed that the concentration of Zn, Pb, and Cd decreases with depth whereas the enrichment in elements of the lower reach increases gradually towards the old sediments. Dijkstra, et al, 2004, characterized the leaching of heavy metals using a batch pH static leaching experiments. The leached concentration of the heavy metals were generally much lower than the metal concentrations and showed a strong dependency on pH, resulted in “V-shaped" leaching curves with order of magnitude changes in solution concentration. Sauve, 2000, concluded that the release of heavy metal cations to water phase "leaching" and so the susceptibility for transport process depends on their solution speciation and their affinity to bind to reactive surfaces in soil matrix and pore water such as particulate and dissolved organic matter, clays, or metal (hydro) oxide surfaces.

Suneela, M., 2004, studied the mobility and transport of heavy metals in Hussain Sagar lake sediments using Tessier sequential extraction scheme. They used microwave heating instead of conventional heating in the sequential extraction procedure and indicated that there is a good agreement between the two techniques for all the metals. The order of the heavy metal concentration in the studied sediments was Zn > Pb > Cu > Ni. The precipitation of heavy metals may be attributed to alkaline pH, as their insoluble hydroxides, oxide and carbonates. Metals like Cr, Cu, and Ni interacted with organic matter in aqueous phase and settled down resulting in high concentrations of these in sediments. Mineralogical studies of polluted sediments indicated that heavy metals are found associated with fine particles of silt and clay size which have longer surface area and tendency to absorb and accumulate metal ions due to their inter molecular forces (Pande and Sharma, 1999).

Metal can dissolve directly into river water from metal scrap yards located along the river and abandoned barges metals can be indirectly released into the river by surface runoff and /or metal contaminated ground water directly from site facilities, such as metal manufacturing plants (Warner, 1998) and transported in the river by binding to suspended sediments. Eventually, heavy metals settle into sediment, filter down into sediment pores, and equilibrium is established at the sediment-interstitial water interface.

Grabowski, et al., 2001, extracted metal to provide important information regarding metal availability in anaerobic sediment. SEM and AVS concentrations were obtained by the cold- acid purge and trap technique during spring and summer seasons along the Mississippi river flood plain. AVS concentrations were significantly greater during summer than spring, resulting in significantly lower SEM-AVS (Simultaneously extracted metal- Acid volatile sulfide) values in summer. SEM-AVS values were found greatler than one at each location during both seasons. Hudson, et al., 1996, studied process of formation and distribution of Pb, Zn, Cd and Cu bearing minerals in the Tyne Basin, Northeast England. Rao, et al, 2001, studied heavy metal distribution in zooplankton and water of the Viskhapatnam harbor, East coast of India (Bay of Bengal). High concentrations of dissolved metals in water and zooplankton were observed at inner harbor water than that of outer harbor waters. Inner harbor was highly polluted due to its proximity to the discharge of metal in industrial effluents along with domestic sewage composed to outer harbor. Moreover, dilution of these effects at outer harbor in contact with coastal seawater of Bay of Bengal by mean of tidal flushing. Duzzin, et al, 1988, sampled sediments and macrobenthos communities to show as pollution indicators for heavy metals in the river Adige (Italy). Macrobenthos preferentially bioaccumulate some metals (Cu, Zn). They found very high concentration of Cr in sediments and macrobenthos due to pollution caused by leather tanning industries. Turiel, et al, 1995, monitored pollution levels in surface water, river sediments and vegetation of La Rioja, Argentina and found high contents of heavy metal in these matrixes. The metal concentration in surface sediments of Dal Lake (Srinager) may be due to the geochemical back ground levels since there is no metal-based industry in the catchment area (Shah, et al, 1988).

Joseph, 1987, studied the heavy metal pollution in the sediment of Cochin estuary. It was found that in the estuarine environment 5-10% of total Cd was potentially available to the biota. The Hooghly river is polluted mainly by industries and intense human activities, and the concentration of Cu, Fe, Mn, Pb and Zn in six macrobenthic mollusks collected from Hooghly river were appreciably high (Abhijeet and Amalsh, 1993). Presence of high toxic metal ions in natural water is subject of serious concern, when such water resources are used for drinking purposes. Prolonged use of metallic contaminated water resources for drinking purpose is dangerous to public health. Mule and Patil, 2001 studied the metal contents in water resources from Radhanageri forest and found that most of the metal contents were in permissible limit. Ground water is a replenishable resource and considered to be least polluted as composed to other inland water resources. Water quality reflects the ingredients present soil through, in which water flows the industrial effluents effect the ground water quality, which is not useful for drinking purpose. Polluted ground water is the cause for spread of epidemics and chronic diseases to human beings.

Some of the detrimental effects attributed to heavy metal ingestion include cadmium poisoning in the Jintsu river, Japan (Shimizu, 1972) and mercury poisoning in the Minamata Bay (Kutsuna, 1968). In Nigeria, It has been reported that fertilizer company at Onne in rivers state, discharge of untreated waste water into Okirika River, (FEPA, 1991), which, affected the aquatic life in the river especially on the fish, and the effects may be transferred to the inhabitants on consumption of these fishes from the river. Alinnor, 2005 reported elemental contamination in water and fish samples from Aba River. The elemental toxicants like Zn and Mn were identified in appreciable amounts in fresh fish species namely, Lates niloticus and Oriochronis niloticus, of mean values 8.012 ppm and 0.861 ppm respectively. The level of elemental contaminates As, Zn, Hg and Mn from the water samples have mean values 0.082 ppm, 11.284 ppm, 0.201 ppm and 1.024 ppm respectively.

It is well known that heavy metals accumulate in tissues of aquatic animals and therefore the levels measured in tissues of aquatic animals can reflect the past exposure (Kalay et al., 1991). Levels of Pb, Cu, Ni, Zn, Mn and Cd in the Kidney and heart tissues of Epinephelus Microclon, collected from the Arabian Gulf, eastern province of Saudi Arabia, were determined by Asraf, 2005. He used wet digestion-based on atomic absorption method. The results indicated that accumulation pattern of analysed metals in the kidney tissues followed the order; Zn > Cu > Pb > Ni > Co > Mn > Cd with Zn at 47.73 $\pm$ 13.26 ppm and Cd at 0.41 $\pm$ 0.16 ppm. In the heart tissues the analysed metals followed almost the same pattern of metal accumulation; Zn > Cu > Pb > Co > Ni > Mn > Cd. The average lead (3.19 $\pm$ 2.03 ppm), nickel (1.6 9 $\pm$ 0.52 ppm), cobalt (1.75 $\pm$ 0.44 ppm), copper (3.96 $\pm$ 0.98 ppm) and cadmium (0.34 $\pm$ 0.23 ppm) concentrations were found high in the heart tissues whereas Zinc and manganese levels were found high in kidney tissues.

Besser, et al, 2004 studied the effects of sediment characteristics on the toxicity of chromium (III) and chromium (VI) to the Amphipod Hyalella azteca. Paul, et al., 1993 studied the trace metals in a tropical river Periyar, Kerala and found that the levels of Zn and Cd in water and sediments increased tenfold in recent years, as compared to a study conducted in 1970. The levels of these trace metals in water increase in summer due to solublisation from the sediment .The trace metals shows maximum concentration at the top layer of sediment column extending up to 20 cm from the surface. Certain heavy metals and the nutrient metals show phytotoxic behavior over a certain limit and hinder the microbial activity in soil. However, their availability and effectiveness in soil is largely governed by a number of factors such as the nature and extent of clay minerals in soil, (Martin, 1972). Mitra and Gupta, 1996 studied the impact of Damodar River and Tamla nala water on soil health and vegetation quality around Durgapur industrial area of West Bengal. They found that effluent irrigated soil was more contaminated with high amounts of heavy metals particularly at down stream than upstream and accumulation of heavy metals in paddy grain was 10-20 times higher than the straw part. Peerzada et al., 1990, determined the concentration of four metals in water, sediments and eight oysters from Gove Harbour Northern Territory, Australia. The measured concentration of Zn, Cd, Cu and Pb, in water were 1.10-7.28, 0.10-2.20, 0.25-3.45 and 0.15 - 2.87 μg/l; in oyster 0.15-123.0, 0.02-0.44, 0.24-2.04 and 4.28- 981.3 μg/g; in sediments 229.98-16053.5, 0.21-7-70, 13.77-50.24, and 759.5-2659.6 μg/g dry weight; respectively.

Conclusion

Heavy metals are very dangerous pollutants owing to their bioaccumulation and toxicity. Therefore, there is an increasing need of determining the metals at trace levels in coastal ecosystems, which directly influences the biological processes.

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