THE EFFECT OF TOXIC SEDIMENTS ON AQUATIC ECOSYSTEM

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Abstract

Various contaminants in sediments of aquatic bodies have a wide range of availability depending on different factors. The toxicants are transported through food web, either by detritus food chain or by grazing route to higher organisms, including man. Studies towards transport, distribution, accumulation and possible beneficial or detrimental impacts of sediments have got high priority during last decade in developed countries. In India, information on this aspect is rarely available in literature. In view of this, present paper reviews the source of sediment pollution in India, the phenomenon of exchange, toxicants in sediment-water interface mobilization of contaminants and gap of knowledge in this area of research.

Key words: *Mobilization, heavy metals, sediments toxicity, suspended particulates.*

Introduction:

Sediments and suspended particulate matter play an important role in the dynamics of inorganic and organic compounds in the aquatic environment. Adsorption of biogenic and pollutant molecules into particles and subsequent deposition means that sediments may act as a temporary or long term sink for many such compounds. The presence of specific compounds in sediments which were discharged from the source of these chemicals indicates long range transport in the environment. Resumption of contaminated sedimentary material and subsequent transport to more pristine areas result in dispersal of pollutants over a much wider region than was initially affected. Furthermore, chemical compounds in sediments may undergo a wide variety of biological and geochemical transformation processes, which may significantly alter molecular structures and distributions.

Recent report and current work indicate a high degree of correlation among suspended sediment organic carbon, nitrogen (N), phosphorous (P), heavy metals and organic residues. The transport, distribution, accumulation and possible beneficial or detrimental impact

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of sediments have been studied from many different viewpoints. One concern during the past decade has been the possible toxicological aspects of sediments, primarily due to their binding and release mechanisms associated with many potentially hazardous trace elements. Water chemistry may be used to determine the various chemical components, and some biological evaluations may be made through relatively straightforward tests. However a major problem still exists with the measurement and evaluation of the toxicological aspects of persistent chemical like heavy metals associated with sediments.

Contaminants in sediments have a wide range of availability depending on lotic, lentic, estuarine or marine conditions, physical properties of the sediments, nature & form of contaminants, and the chemical & biological parameters of the waterinvolved. One of the major problems encountered with measurement and evaluation of toxic contaminants in sediments is that contaminants rarely occur alone. Further it has often been encountered with a contamination of different contaminants with a varied ratio of chemical speciation. These combinations may exert a synergistic or antagonistic effect on aquatic organisms exhibiting widely varying effect amongst species towards tolerance or susceptibility to pollution. However the analysis of most toxic contaminants are performed for each individual element and require some type of evaluation as to the detrimental or protective effects of the combined metals.

Amongst different type of toxicants associated with sediments in lotic and lentic aquatic bodies of India, the most persistent hazardous elements are heavy metals. Since scientific study towards sediment toxicity has not been prioritized in India, present state of art delineates a brief account of existing knowledge on source of heavy metal pollutants, mobilization of the metals, adverse impact of the toxicants to aquatic food chain organisms and future studies needed on this aspect

Sources of heavy metal contaminants:

Sediments contaminated with toxicants primarily accumulate in the bed of a lentic or lotic water body through different sources as stated below.

- Ø Municipal wastewaters
- Ø Immersion of idols & municipal solid wastes
- Ø Diffuse non-profit product
- Ø Coal fired power plants
- Ø Urban runoff
- Ø Mine waters and operations
- Ø Various industrial wastewaters
- Ø Weathering

Anthropogenic sources clearly dominate in the number of sources and in total loading to most system

Heavy metals within the sedimentary system

Following disposal of waters, heavy metals commonly find their way to the sediment of h their tendency to enter into complexation and sorption reactions with solid phases. Hydrous oxides of Fe and Mn are among the most important sorbing agents for other metals. Heavy metals have also frequently been associated with organic and elastic suspended solid. Their reactions depend not only on the availability of interacting solids, but also on the various chemical conditions within an ecosystem, most notably pH and oxidation reduction state. The residence times of heavy metals in the water column above the sediments is a function of the occurrence and rate of the above interactions and probably more importantly, the magnitude of the water movement. Thus longitudinal transport within lotic environments generally exceeds that within lentic system.

Both lotic and lentic benthic sedimentary systems repeatedly have been found to be enriched in heavy metals. Thus the transfer of trace elements into the sediments generally exceeds the transfer out. Some of the most spatially comprehensive data on heavy metals within lotic sediment have been obtained in Great Britain by Thomton *et al.*.They found that the heavy metal contents of stream sediments were useful in predicting the status of associated waters with respect to these materials. A large number of investigations have assessed sedimentary trace elements levels and distributions to reflect anthropogenic metal loadings. In lotic environments, there is a differentiation between active and bank stream sediments, since seasonal and storm runoff frequently results in the transport of heavy metal rich sediments to downstream reservoirs and lakes.

Knowledge of the form and behavior of trace elements within the sedimentary system can yield insight into the circumstances by which these materials can be released back into the overlying waters. Heavy metals are often found to be preferentially associated with smaller particle sizes and organic, fractions. These fractions are characteristically associated with the deep water portion of benthic systems. Apparent anomalies in the horizontal distribution of trace elements may often be negated through normalization of the composition of sediment size fractions. Differential extraction procedures are commonly executed to gain insight into the relative availability of different metal forms. For example, malo and Agemian and Chore used different leaching agents to separate adsorbed metal forms from those forms incorporated in crystalline structures. Both works concluded that 0.3 – 0.5 N HCL extraction effectively leached adsorbed metals, while 4.0 N HNO_3 attached mineral lattices. Helsinger has argued that metals extractable by hydrogen peroxide are organically bound and acetic acid extractable represents the exchangeable phase. Another approach in evaluating the availability of trace elements in sediments has been the delineation of the relative uptake of elements (in soluble form) by the various fractions common to sediments. As an example, mercury uptake was preferentially sorbed to the smaller particle size fraction. These phenomena are highly pH and oxidation reduction state dependent.

Mobilisation of Heavy Metals From Sediments

In general, it may be said that the major fractions of trace metals are typically strongly bound within the sedimentary system, with only relatively small fractions being mobilized by other than physical means. This has been documented in a number of lentic systems, based on extensive stratigraphic characterization of core samples that included dating techniques. The vertical distributions of trace elements were ground to be consistent with historical data concerning the system's anthropogenic developments and measured sedimentation rates. Exceptional vertical mobilization within the consolidated sedimentary layers (remote from the partially mixed surface sediments) of lentic systems has only rarely been reported and is probably explainable based on ecosystem – specific peculiarities.

The two-directional exchange does occur across the sediment interface. The magnitude of exchange, in either direction, is clearly dependent on both the character of the sediments and the overlying water. Thus, the exchange of trace element can be viewed us gross type of equilibrium, where the movement to the sediment is favored for nearly all systems. The ratio of the sedimentary inputs to losses to the water column probably varies greatly from ecosystem to ecosystem. Since factors that affect exchange can vary substantially with time for a given ecosystem, the equilibrium is dynamic in nature.

Some of factors that influence the exchange of materials (including trace elements) between the sediments and overlying water are summarized below.

Physical factors

- Temperature
- Hydrodynamics and mixing

Chemical factors

- Acid- base
- Complexion
- Oxidation – reduction
- Sorption – desorption
- Precipitation – dissolution

Biological factors

- Food web
- Migration
- Bioturbation

Physical factors

Temperature:

Temperature influences are particularly to the various reaction rate kinetics for the above listed biochemical and chemical transformations, in the north temperate climate. The seasonal changes in lotic environments typically exceed those for lentic systems. Investigations for sedimentary exchange reactions are apparently lacking.

Hydrodynamics and missing: detailed studies on the hydrodynamics of natural waters and sediments as they might affect sedimentary water exchange reactions are generally lacking. Lee[16] indicated that the hydrodynamics of the systems are often the rate controlling steps in sedimentary exchange reactions. Current in the overlying waters tend to transport leached material away from the sediments and thereby allow concentration, -dependent (concentration gradient exchange) reactions to proceed. However, mixing the overlying waters promotes sedimentary particle suspension, which in the surface sediments carries un leached particles and interstitial water to the sediment – water inter

In lakes, mixing in the water and sediments arises primarily from wind – induced currents and physical activity of larges organisms. Bryson and Kuhn conducted a bottom current study for lake. Mendota and estimated currents as high as 10 cm/sec near the sediments under high wind conditions during thermal stratification periods. Bottom currents of several cm/sec wee also reported for ice – covered lakes. Bottom water currents are no doubt temporally variable for a given system with ranges for different systems that depend on ecosystem – specific characteristics such as morphology. The magnitude of barroom current and surface sedimentary mixing may often be limiting exchange in lentic systems. This has been evidenced by the large chemical gradients that are typically present in the waters directly above the sediments, particularly in eutrophic systems. In addition to affecting the rate of exchange the mixing in sediments also dictates the depth of sediment that may ultimately become involves in exchange reactions estimates of mixing depths vary from approximately 1-2 mm thick for the highly compacted sediments of hyper eutrophic Onondaga lake20. Data from 96 lakes in Norway were used by Boyle and briks to model heavy metal concentrations in lake sediments in relation to atmospheric deposition. The KD (distribution coefficient of the metal between particles and waters) values for Cd and were estimated as 105.8 and 106.2 respectively. Biogenic silica influenced Kd values for Pb, and Zn, whereas for exchange is much greater for the more fluid sediments.

The mixing in rivers and streams arises from the flow of water due to differences in elevation of the land through which the rivers and streams flow above the sediments and relative mixing within the surface sediments are substantially greater than for lentic systems. Qualitatively not only should this accelerate the relative rate of two-phase exchange, but it also results in substantial transport of (possibly contaminated) sediment. The association of trace elements with the smaller particle fraction implies that physical mobilization is to be expected. Several studies by jennet and co-workers 22 demonstrated that runoff transport is a major factor for movement of heavy metals in lotic systems. In one of the study which the form in which most of the mass of metals were transport is a major factor for movement of heavy metals in lotic systems. In one of the studies the form in which most of the mass of metals were transported varied: Cd was almost completely a solubilized, Pb was generally a particulate; and Zn was approximately one half dissolved. Thus, lentic systems, which may be remote from direct trace element contamination but which receive tributary flow from streams with contaminated sediments, can be expected to represent a long term sink for these materials.

Chemical factors:

According to lee16 the chemical factors that may influence exchange reactions include the chemical characteristics of the water and sediments and the chemical transformations that lead to exchange. In overall exchange reactions, number of chemical reaction types, as mentioned below, may play an important role.

Acid base:

since many chemical reactions are pH-dependent, acid – base reactions can affect exchange reactions in a number of ways. Natural water sediments normally do not show large pH changes because they are usually well buffered due to the presence of large amounts of clay materials, particulate organic matter and, in calcareous systems, precipitated calcium carbonate. In lentic systems, the pH of overlying hypolimnetic waters may drop as much as two units during stratification periods. Highly productive shallow streams may experience daily pH variations in the range of 6-9, coincident with dark and light periods respectively. In sylvas23 description of the aquatic chemistry of copper, the critical role of pH in affecting not only complexation, but also the rate of adsorption gas been demonstrated. he influence of pH and redox Potential (Eh) on solubility of Ba from barite and phosphogypsum (PG) in Louisiana Mississippi river alluvial sediment was examined by Carbonell *et al.* Approximately 4.4% of the total native Ba present in the sediment was converted to a soluble form under acidic and 0.3% under alkaline and either anaerobic or aerobic condition. PG application to the sediment significantly reduced the level of soluble Ba compared to control sediments. Further, adsorption capacity for cationic heavy metals, eg. Zn, Ni, Cu and Pb, commonly decreases with pH resulting in an increased solubility of these heavy metals with depth in the oxic and suboxic layers. Besides organic matter degradation dissolution of hydroxides promotes release of heavy metals to the pore water. In such circumstances increased pore water concentrations of heavy metals were observed directly below the sediment water interface.

Complexation:

In the light of the presence of various organic compounds common to freshwater, complexation reactions can be important in sediment water exchange processes which have high trace element complexing capabilities. These reactions can be heterogeneous or homogeneous. The formation of a complex in solution acts to enhance the exchange from the sediments because the complex tends to drive the reaction towards the solution phase. complexation with solids has the opposite effect. Fulvic and humic acids derived from various natural sources including decomposed leaf litter and planktonic organisms are common to all freshwater systems. The levels of these organic acids are ecosystem- And season - specific. Laboratory studies 26-28 have indicated that both fulvic and humic acids are highly potent-in the mobilisation of sedimentary trace metals. However, field investigations of this interaction have been rare. Other chelating organics, such as EDTA, NTA and other detergent sequestering agents have been found29 to have high mobilization potential, some of which may be anticipated in eater receiving municipal waste treatment effluents. The methodology for in situ evaluation of these interactions is not presently available.

Oxidation-Reduction:

Overall redox state of the mobilization of trace elements. As the redox-potential drops. The mobility of the sedimentary trace metals generally increases. Considerable efforts have been made by investigators to quantify overall oxidation reduction characteristics of lentic and lotic waters and their sediments by measurements of Eh using platinum or other noble metals electrodes. These measurements are only crude estimates of the overall oxidizing and reducing conditions and are nor used to predict the ratios of oxidized to reduced species. Aerobic environments are normally oxidative, while anaerobic are reducing. Subsurface sedimentary layers are reducing in most cases, while surface sediments and overlying waters are typically oxidative. This latter situation may not be the case for the hypolimnetic systems, which may become anaerobic periodically these conditions would be much more unlikely in lotic systems.

Desorption-sorption:

sorption reactions are one of the most important types of reactions controlling the exchange of materials between sediment and water. Sorption is pH dependent fast process and also somewhat reversible. Studies reveal that sorbed trace metals can be released to the water, particularly under low pH and high ionic strength conditions 11,22,31.further work on desorption is required to identify mechanisms and quantify the transformation.

Precipitation-dissolution:

precipitation reactions contribute to the deposition of trace elements in the sedimentary system. The trace elements that are incorporated in amorphous or crystalline precipitates are tightly bound or occluded farms, which would not be expected to be readily mobilized under conditions composition. Substantial dissolution would be anticipated only under drastically altered ionic strength and composition conditions, that might be expected from a major reclamation effort.

Biological Factors

Biological activity within the sediments results in physical mixing through the movement of macro benthic forms of through gas release associated with microbial stabilization process. The biota may further influence the exchange of trace materials through direct or indirect mechanisms. Several bacteria common to aquatic ecosystems are capable of transforming rather immobile forms of Hg and Pb to highly mobile ones through methylation processes32,33. The chemical characteristics of the water changes as a result of photosynthetic and respiratory activities, particularly by microbial populations, pH, ionic strength and oxidation – reduction potential which can all affect the magnitude of exchange. Based on the highly insoluble nature of many metal sulfides, the reduction of sulfate to sulfide by certain certain bacteria is significant in some systems. Mobilization of trace metals, through biota can be summarized as fallows:

Food web:

heavy metals in sediments react differently under the physical, biological and chemical factors. Inorganic mercury may be converted to methyl of dimethyl mercury by anaerobic bacteria found in the bottom muds of stream, rivers or lakes. The methyl mercury is soluble in water and therefore more availability for incorporation into the tissues of organisms with the resulting possibility of bio concentration up the food pyramid, ultimately to man. Lead continues to be another element of concern as to the chemical speciation or amount found in sediments. Zinc is an essential element for plant and animals but may become toxic to some animals at levels exceeding 900 ppm29 most toxicity problems encountered with toxicity problems encountered with zinc. Cadmium appears to be highly toxic to aquatic organisms in the 0.02-2.0 ppm rabge30 whereas 4 ppm in the diet of humans is normally considered toxic31 copper is the most common heavy metal to which aquatic organisms are exposed, based on its common use as an algcide. The continued ingestion of copper may lead to accumulation in lever. Chromium levels in sediments are usually associated with man-induced pollution. Trace elements toxicity in sediments sediment remains a matter of bioavailability under different physical, biological or chemical conditions. Most of the toxicity research in aquatic ecosystems has been concerned with the amount and for of materials present in water of aquatic life, what is needed is to quantify the amount of potential toxic material bound up in sediments.

As part of an overall assessment of possible adverse effects of heavy metals originating from coal-fired power generation, laboratory-scale physical models (microcosms) were used to determine aquatic ecosystem responses to specific heavy metals (Zn, Cd, Cr, pb and Hg) at trace levels. The microcosms were designed to simulate lake powell in south-eastern Utah and northern arizona as the final environmental sink for the stack emitted heavy metals. The overall results of the study indicate the lake powell microcosms were significantly affected by elevated metal concentrations. The algal populations were effective in reducing metal to lower levels removal rates were related to soluble metal concentration and pH. The removal rates for Zn were comparable to the sediment removal and revealed the ability of algae to remove high levels of metals. One of the major potential problems associated with marsh development is the mobilization of contaminants from dredged material. If the contaminants are absorbed and trans located to the aerial positions of plants, they may be passed along the estuarine food web through either the detritus food chain directly through grazing by herbivorus invertebrates, water fowl and small mammals. The extent to which uptake into the into the aerial portion of the plants occurs probably depends on the type of dredge material. Rooted aquatics may concentrate pollutants from the sediments, as demonstrated by the high concentration of mercury in spartina alterniflora. Available evidence suggests that rooted aquatics more often pump pollutants from sediment.

Several investigations have interpreted the ability of benthic invertebrates to accumulate pollutants in terms of their feeding type or tropic position. Phelps et al. examined the distribution of stable elements among polychaetes off the West Coast of Puerto Rico/ they found that nonselective deposit – feeders had consistently higher Zinc concentrations, while the concentration of Iron, Samarium and Scandium were highest in filter-feeders and selective deposit-feeders. These relationships refoected the distribution of the elements. Inc was more available in the interstitial water of sub-surface sediments, while Iron, samarium and scandium were found in particulate matter at the sediment-water interface.

An important aspect of the trophic transport of pollutant within benthic ecosystem that should be emphasized in future research is the contamination of detritus food chains. A variety of main macro algae and spermatophytes are known to trace metals, from sediment, often with very high concentration factors. Similarly seeliger and Edward reported that the majority of dissolved inorganic copper taken up by the red algae ceramium pedicellatum and Meogardhiella baeleyi will eventually become available to consumers, either as particulate detritus or dissolved organic matter. Only a small portion (<10%) of the copper is recycled in dissolved inorganic form. In their exemplary study of metal distribution in an eelgrass (*Zostera marina*) community, *wolfe et al.* estimated that 55% of net eelgrass productivity is consumed as detritus by macrofaunal benthos.

Thus the literature provides strong evidence that plants accumulate concentration of pollutants and that benthic invertebrates are the principal consumers of contaminated plant detritus. Laboratory microcosms that stimulate detrital food chain could provide a useful research tool for comparative study of pollutant dynamics within benthic ecosystems.

Migration: migration, in this case, is the sense of spatial movement of animals entering or leaving areas of sediment contamination of seasonal, migrations in estuarine and coastal waters have been described for a tremendous variety of demersal fishes and epibenthic invertebrates. Bacis believes that dispersal from crowded or deteriorating habitats is the most lidely explanation of the nocturnal movements of benthic invertebrates.

The contribution of migration to the flux of pollutants within ecosystems has rarely been examined. *Wolfe et al.* Found that the total amounts of Mn, Fe, Cu and n involved is the seasonal migrations of fisher and invertebrates represents only a 'minute fraction' of the annual sediment accumulation of these metals within eelgrass (zostera) beds. The body burden of diurnally and larger proportion of the pollutant pool available to higher trophic levels through predation. Migrating animals may be the first colonizers of disturbed habitats.

Bioturbation :

The time required for macoma balthica , a bivalve, to reburroq was greater in sediments containing high levels of heavy metals. Reburrowing time of various bivalves inc result in response to the water – soluble fraction of crude oil dissolved copper. Avoidance of polluted sediment by aquatic invertebrates40 may result in lover bioturbation rates in patches of pollutant sediment.

Effect of the suspended particulates on aquatic organisms

Relatively few studies of the direct effect of elevated suspended solids concentrations on aquatic animals are available. Among the invertebrates, most work pertains to mollusks of crustaceans. The effects of many kinds of particles, including a variets of processed clay mineral, fuller's earth, powdered chalk, incinerator ash, coal washings and glass shard, have been studied. Several investigations have used natural sedimats taken directly from aquatic deposit usually, sizing , drying or otherwise altering their physical, chemical and biological properties before using them in experiments.

Cordon and kelley concluded that adult freshwater organism could probably tolerant the normal extremes of suspended solids, but that deposition would kill eggs. Larvae and insect fauna and would alter the characteristics of the bottom, wilber concluded that most filter feeders are not affected below a certain concentration, but that higher solids concentrations interfere with filtering mechanisms. He also speculated that a given suspended solid concentration interfere with filtering mechanisms. He also speculated that a given suspended solid concentration might be more harmful in normally very clear water than in usually muddy water.

Sherk discussed the concept that each environment has inherent physical, chemical and biological limits, beyond which significant effects will occur, and that suspended and deposited sediment affects living systems in many different ways. Kunkle and comer showed that turbidity could be related to weight per volume concentration of particles only if all the particles were of uniform physical and chemical nature and instruments were calibrated against weighed samples. It is revealed that the response of organisms may not be due to mass concentration of suspended solids, but perhaps to the number of particle in suspension and their densities, sie distribution, shape and mineralogy, presence of organic matter and its form, and metallic oxide coatings or sorptive properties of the particles.

Conclusion

Toxicity and bioaccumulation tests with benthic invertebrates are a common and efficient method for assessing potential impacts of sediment associated contaminants on aquatic ecosystems. The results of biological tests with sediments are used in a decision making framework for marine and freshwater dredge material disposal programmes in the United States48 ,49 and it appears highly probable that the for decisions made in other types of regulatory programmes, including pesticide and point - source discharge permitting, and relater remedial activities effect-based i.e. biological testing, has several advantages over simple chemical analyses as a basis for regulatory decision making. These advantages include an enhanced ability to assess the potential toxicity of complex mixtures of chemicals and to account for differential bioavaiability of contaminants in varying matrices . At workshops sponsored by the U.S. Environmental protection Agency (EPA), three species of benthic invertebrates were identified as promising for the development of standardised tests with freshwater sediments: the amphipod hyalella azteca and the midge chironomors tentans for toxicity toxicity testing, and the oligochaete Lumbriculus variegates for bio accumulation testing50 . All three species have been used relatively frequentl for assessing freshwater sediments51 . However, sediment toxicity had not been considered while deriving standards for discharging the wastes in Indian surface waters.

In determining the health of a particular aquatic habitat, the bulk of the investigative work has been concerned with the chemical quality of the water column and the biological community . the elutriate procedure is deficient because it addresses only the immediate impact of sediments of the eater column and ignores the immediate impact of sediments of the water column and ignores the impact on the benthic community.

Temporal database towards sources of sediments, quantification of disposal at different lotic and lentic environments, mobilization of the toxicants to the toxicants to the water phase and abiotic changes need to be generated and/or various water bodies of India. Acute and chronic bioassays, coupled with uptake studies of the test orgarisms should be conducted to further delimit this gtay area. It is also possible that investigations of the synergistic and / or antagonistic effects of several chemicals, particularly the heavy metals, in spiked samples would lead to a better understanding of the complex combinations of pollutants found in natural systems and their effects on the biota.

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