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Role Of Detritus On Trace Metals In Wetland-Terrestrial Systems: A Review



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ABSTRACT

Mass settling of the detritus through the overlying water column results in their accumulation at the bed surface of aquatic bodies (wetlands, lakes, ocean etc.). This review attempts brief description about the processes that start soon after the deposition of detrital matter resulting in formation of relatively stable end product, the humus that plays a major role in pedochemical processes. This review discusses the interaction (Complexation) between humus (Natural organic matter in soil/sediments) and trace metals, which determines their fate in aquatic systems, specifically wetlands. The activities of metal ions at the binding sites, the common methods used to study complexation of humic substances with metal elements are also talked over. The limitations of the instrumental methods in studying the complexation process and its possible solutions are focussed in this section. In this context certain aspects of trace metal (Bio) availability, distribution and mobility are also discussed. In addition, this review provides a brief overview of chemical speciation of trace metals in the system.

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KEYWORDS

Complexation;
Detritus;
Fulvic acid;
Humic acid;
Humus;
Speciation;
Trace metal.

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INTRODUCTION

Wetlands (A major feature of landscape in almost all parts of the world) are among the important ecosystems on Earth. As per the Ramsar Convention (IUCN), 'wetlands are areas of marsh, fen, peat land or water, whether natural or artificial, permanent or temporary, with water that is static or flowing, fresh, brackish or salt including areas of marine water the depth of which at low tide does not exceed 6 meters'^[1]. They perform a number of valuable functions and provide several services and commodities to humanity and thus are ecologically unique^[1-9]. The single most important factor that determines the conditions of a wetland is its hydrological regime, which directly modifies or changes the chemical and physical properties such as nutrient availability, degree of substrate anoxia, soil salinity and pH^[10-11]. These modifications of the physico-chemical environment in turn have a direct impact on the biotic systems in the wetland. When hydrologic conditions in wetlands change even slightly, the biota may respond with massive changes in species composition, richness and ecosystem productivity.

Sediment is composed of a combination of lithogenic, authigenic, and biogenic components such as mineral grains, organic matter, Fe and Mn oxides, sulphides, and carbonates^[12]. It is generally referred to those materials that are deposited by natural processes. But when it is related to wetland, it can be fluvial as well as alluvial. The former one refers to the already existing material in the bottom layer of aquatic bodies (wetlands, lakes, ocean etc.), whereas the latter one refers to those materials carried by rushing streams and deposited where the stream slows down. But sediments differ from soils in many aspects; with moisture/water availability being the major factor that results in the differences. The major difference between these two is in the rate of decomposition and hence the organic carbon turnover. However the differences can be less especially in case of riparian ecosystems/wetlands, ecosystems with a high water table because of proximity to an aquatic ecosystem or subsurface water^[1]. They usually occur as an ecotone between aquatic and upland ecosystems but have distinct

vegetation and soil characteristics. Continuous interactions occur between riparian, aquatic and upland terrestrial ecosystems through exchanges of energy, nutrients and species. The common characteristic of all these things is that they are continually in a state of change. Therefore both soil as well as sediment is essentially dynamic.

In any wetland system, the sediment remains saturated with water most of the year except for instances, where water becomes scarce during summer months during which the lakes or wetlands become dry. Some wetlands can have high hydrological throughput (minerotrophic), whereas others are fed mainly by precipitation and have low hydrological throughput (ombrotrophic^[13]). This variation in hydrology has implications for ecosystem function. Minerotrophic wetlands utilize nutrients from outside and nutrients can be washed off from them easily. Ombrotrophic wetlands must rely heavily upon nutrient input from precipitation and internal nutrient cycling. Autochthonous production in wetlands is a major source of organic matter. In wetlands water dynamics have profound influence on the genesis of soils. As a result of water saturation, O₂ diffusion into soil is drastically curtailed. The O₂ trapped in the soil or present in the water is consumed within few hours by microbes. The resultant waterlogged soil is practically devoid of molecular O₂ creating a specific redox conditions. As long as molecular O₂ is available it acts as the preferred electron acceptor, followed by NO₃, Mn oxide, Fe(hydr) oxides, SO₄ and finally CO₂^[14]. Reduction of the different acceptors is accompanied by typical ranges of redox potential (E_H), and measurement of E_H can be used to quantify the tendency of the medium to oxidize or reduce substances.

In wetlands, sediment is a site for many processes including nutrient cycling. Both the sedimentary as well as the gaseous cycles operate through it, as being the storehouse of organic matter and nutrients. Organic matter influences physical and chemical properties of the soil or the sediment and it commonly accounts for 35-40% of cation exchange capacity (CEC, cmol/kg), of soils/sediment and is highly responsible for the stability of the soil/sediment aggregates.

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Detritus decomposition and humification

Organic carbon accumulation in wetlands is the net result of primary production (carbon fixation) and decomposition (carbon mineralization^[15]) of dead and decaying plant and animal debris, the detritus, followed by synthesis of new simpler materials by soil microbial population^[16]. The major source of detritus (organic matter) in wetlands is mainly plant tissue, mostly hydrophytes. However materials of animal origin also contribute. Animals, usually considered secondary sources of organic matter, contribute waste products and their own bodies as their life cycles are consummated. Under natural conditions, the tops and roots and even the whole plant body of hydrophytes and other native plants annually supply large quantities of organic residues. Under certain conditions, phytoplankton as well as hydrophytes from surface waters may aggregate, settle rapidly through the water column, and accumulate, relatively intact, as phytodetritus on the floor. These detritic materials generally form a layer in the bottom, which is clearly distinguishable from the earlier layers of the profile. The first rigorous definition of phytodetritus was that of Odum & De la Cruz^[17], who stated, 'phytodetritus is the particulate material originating from decomposing vegetal biomass'. Though by definition phytodetritus refers to the materials of vegetal origin, it also contains proto and zoogenic detritus^[18-19]. As these organic materials are decomposed and digested by benthic microbes, they become part of the underlying sediment. The organic residues provide food for benthic organisms, which in turn create stable compounds that help maintain the organic level of the soil/sediment system.

The residence time of the detritus, the period required for its complete decomposition, depends on (1) its quality and composition, (2) the extent of microbial activity, (3) the prevailing environmental conditions and (4) the frequency of resuspension. If the quantity of the detritus deposited is greater than that the benthic community can process (processing capacity), a 'fluff' layer distinct from the underlying sediment may develop on the floor of the aquatic body^[20]. The fluff layers on the deep-lake floor can also be composed of faecal pellets^[21] or unconsolidated

sediment^[22-23]. Detritus may also be resuspended and advected laterally, forming a major source of near-bottom suspended matter in aquatic bodies such as wetlands, lakes etc. The resuspension of detritus increases its residence time above the sediment-water interface, delaying burial and enhancing remineralization^[24]. Vertical resuspension may also be possible due to seasonal water circulation, which can alter the chemistry of the overlying water column as well as the bottom sediment.

The extent of mixing of the detritus with the bottom profile (sediment/soil) in the case of wetlands as well as terrestrial systems depends on the rate of decomposition that vary greatly almost in the order of sugars, starches and simple proteins > crude proteins > hemicelluloses > cellulose > fats, waxes, etc > lignins^[25]. All organic compounds (detritic materials) usually begin decomposing as and when they enter the system. The sugars and simple proteins decompose most readily; at the other extreme lignins are the most resistant to breakdown. Generally lignin and cellulose are said to be the defining components of the 'carbon quality' of an organic substrate, as they are resistant to degradation. Although lignin is more resistant than cellulose to decomposition, their decay rates are approximately the same under aerobic conditions unlike in anaerobic conditions (in aquatic systems), where degradation of these compounds is slow. Thus initial substrate composition can be used as a predictor of decomposition and expected organic carbon dynamics. The decomposition results through various intermediate components in a number of simpler entities, like carbon dioxide and others such as nitrogen, sulphur and phosphorus. For example, proteins are decomposed into amino acids, which in turn are broken down to produce first ammonium compounds, sulphides and then nitrates (nitrification) and sulphates. Similar breakdown of other organic compounds releases inorganic phosphates as well as cations such as Ca^{2+} , Mg^{2+} and K^{+} . This overall process, the mineralization, immediately follows decomposition.

The decomposition of organic matter is governed by other external or environmental factors^[26]. Studies based on the detritus food webs^[27] associated with buried litter have indicated that such systems are more

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bacteria dominated, while surface litter systems are more fungi dominated. Unlike terrestrial ecosystems, decomposition in wetlands is frequently electron-acceptor-limited. In addition to oxygen, alternate electron acceptors for anaerobic microbial respiration, such as NO_3^- , Mn^{4+} , Fe^{3+} and SO_4^{2-} , are often in short supply relative to the demand created by organic carbon, resulting in the formation of methane, a process known as methanogenesis as the principal microbial respiration pathway.

Humus

Humus, a dark coloured, amorphous and rather resistant product of plant and animal matter decomposition is an integral component of any natural system such as water as well as soil. Because of its resistance to degradation, prevailing environmental conditions (unfavourable for decomposition) and insolubility in water it can be referred as refractory organic matter in aquatic systems. But so far as the natural soil system (also the sediment) is concerned it is vital for most of the biological and physico-chemical processes and persists as organic colloids. The process of humus formation, known as humification, consists of two processes: decomposition and synthesis^[25].

Under less than ideal conditions for decomposition, a portion of the litter entering the soil system is not completely decomposed, but is modified into humus, which may decompose slowly and hence accumulate^[28]. The first and most important aspect of humus formation is shredding of organic matter (detritus), which will be performed by saprophagous fauna (earthworms, millipedes, snails, enchytraeids etc.) followed by microorganisms^[29], which will subsequently be subjected to further chemical transformations. It is found that around 90% of the organic matter has been processed by two of these animal groups, enchytraeids and earthworms^[30-31]. According to Aber and Melillo^[32], the decomposition process from litter to humus has two stages. In the first stage, there is rapid loss of solubles (sugars, starches, proteins) followed by cellulose, but a little loss or sometimes-even gain of lignin (insoluble decay products). During this stage, carbon is relatively available and nutrients are

limiting, and there is immobilization of the nutrients such as N. Once the litter reaches the second stage, it can be considered as humus, it has stabilized contents and slow decomposition rate. During the late stage of decay, there is net loss of lignin and N mineralization. The critical determining factor for the rate of humus accumulation on a site is how much of the original litter mass remains at a point at which the materials gets converted to humus and decomposition slows down.

Humus consists of the humic and non-humic group. The humic group, which makes up to 60-80% of the soil organic matter, is comprised of complex and resistant materials characterised by aromatic ring-type structures that include polyphenols and polyquinones, which are even more complex and are formed by decomposition, synthesis and polymerisation as indicated above. The humic substances have no sharply defined physical or chemical properties unlike non-humic compounds. They are amorphous, dark in colour and have high to very high molecular weights, varying from a few hundred to several thousand units. Humic substances are classified into three chemical groups on the basis of their resistance to degradation (residence time in soil) and of their solubility in acids and alkalis (TABLE 1^[25,33-34]). Fulvic acid, the most easily degraded compound, is still quite stable in the soil and is more resistant to microbial attack than most fresh plant materials. Depending on the environment, it may take up to 50 years to destroy fulvic acid type compounds and hundreds of years for humic acid type of compounds in the soil. However, all three humic groups have similarity with regard to the ability to absorb and release cations, and hence are considered together as 'humic materials'.

The non-humic group, comprising about 20-30% of the soil organic matter, are less complex and less resistant to microbial attacks as they are formed of specific organic compounds with simpler definite physical and chemical properties. The compounds coming under this category are polysaccharides, polyuronides and organic acids. These compounds are produced as a result of microbial synthesis.

Elemental composition of humic materials

The humic substances in soil/sediment are

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TABLE 1: Characteristics of humic substances

No	Property	Humic substances		
		Fulvic acid	Humic acid	Humic
1	Molecular weight	Lowest	Medium	Highest
2	Colour	Lightest	Medium	Darkest
3	Solubility	Soluble in both acid and alkali	Soluble in alkali but insoluble in acid	Insoluble in both acid and alkali
4	Susceptibility to degradation	Most susceptible to microbial attack	Intermediate in resistance to degradation	Most resistant to microbial attack
5	Residence time in soil	15-50 years	> 100 yrs	Not known
6	Approximate Chemical formula	$C_{135}H_{182}O_{95}N_5S_2$	$C_{187}H_{186}O_{89}N_9S$	Not known

Source: [25,33-34]

TABLE 2: Elemental composition of humus acids

Sl no	Element	Humic Acid	Fulvic Acid
1	Carbon	46-62	36-44
2	Nitrogen	3-6	3-4.5
3	Hydrogen	3-5	3-5
4	Oxygen	32-38	45-50

The value is the approximate percentage composition(w/w) only
Source:[35]

composed of a mixture of organic molecules hosting a multitude of elements and functional groups, which exhibit widely varying degrees of reactivity. The elemental composition of humus acids is used as an index of the direction of the humification process and for formulating the simplest formulae of humus acids. Both the humic fractions, i.e. humic acid(HA) and fulvic acid(FA) contain common elements like C, N, H, O, S, P and different metal cations^[35]. In general, FAs differ from HAs by a lower content of carbon and higher content of oxygen(TABLE 2). Both fractions contain about 0.1% S, which in exceptional cases goes up to 1-2% and 0.01-0.1% P. S is considered an essential element and is particularly present in the amino acids. Moreover, S is present in the form of adsorption complexes(SO_4^{2-}). Residues of nucleoproteins, inositolphosphates, phospholipids and chemisorbed phosphates represent phosphorus. Metal cations are not the constituents of HAs and FAs; their presence indicates formation of simple or complex salts of humus acids.

In elemental composition, HAs occupy an intermediate position between lignin and carbohydrates, while FAs are close to simpler compounds such as carbohydrates and proteins. The

composition of humus acids(HA, FA and similar compounds) varies with depth in a profile and depends on 1) the type of vegetation of the area, 2) the quality of original organic tissue(mostly litters), 3) the soil texture, and 4) other environmental parameters. The elemental composition of humus acids has been studied by different researchers^[36-38]. Certini's^[37] investigation on the N variability in the humus acids in volcanic soils reported minor differences in N content among the different soil horizons along the depth profile. The investigation by Reintam et al.^[36] on the elemental composition of humus acids in the epipedon of certain estonian soils reported a particularly uniform and stable composition of both humus acids with age differences up to 7,000 years. Though the composition of HAs and FAs were similar, fulvic acids contain comparatively higher hydrogen content. A differential composition of both humus acids with respect to major elements among the epipedon of even different age groups of the same soil, thus showing a temporal variability, was also reported.

In soils humic substances can occur either as organic colloids, or in the gel or solid state. Their physical state is dependent largely on the soil pH, its moisture content and the extent of charge neutralization exerted by the counter ions present in the medium^[39]. Several transformation processes of terrestrial and aquatic organic matter in the environment are connected with various organic free radicals reactions. These free radicals in humic substances(HS) are detected by electron paramagnetic resonance(EPR) spectroscopy. The concentration of organic free radicals in HS is an important parameter

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obtainable by EPR spectroscopy and has been associated with several aspects related to structure and reactivity of these materials. Such a concentration may be used to assess the degree of humification of soil HS, to study the impact of different cropping systems and rainfall on soil organic matter, to estimate HS reactivity and also the fate of metal ions for environmental control^[40]. The humic organic free radicals concentration (HOFRC) depends on a number of environmental factors influencing its production and stabilization, e.g., origin of material, climate, pollution (oxides of sulphur, oxides of nitrogen, transitional metals), pH and redox conditions^[40], irradiation, acid-hydrolysis, methylation and temperature^[41].

Indices of humification

The humus status of soils is described by a wide range of indices reflecting the level of accumulation of humus in the soil, its distribution in the profile, its qualitative composition, formation of organomineral derivatives, and the mobility of the humic substances. The range of indices to be determined to characterize the humus status of soils vary depending on the aim of the investigation. The important indices of the humus status of soils most often used are^[35,42] (i) Thickness of litter (for forest soils), (ii) Ratio of organic matter in the litter and in the mineral profile, (iii) Content of humus in the various strata (%), (iv) Humus reserve in 0 to 20cm (0 to 100cm layer, t/ha), (v) Distribution of humus in 1m of the soil profile, (vi) Nitrogen enrichment of humus based on C: N ratio, (vii) Degree of humification of organic matter $[(C_{HA}/C_{total}) * 100]$, (viii) Type of humus ($C_{HA}:C_{FA}$), (ix) Content of free humic acids (% of total humic acids) and (x) Optical density of humic acids. Of all the above-cited indices, the percentage of C_{HA} in total organic carbon and the type of humus is important and accurate criterion to determine the degree of evolution or maturity of the humification process. Based on the relative distribution of humus organic carbon into classical humic fractions (HA and FA), four types of humus (TABLE 3) can be recognizable. Although this measurement seems to have high potential to indicate different pedochemical processes in terms of

TABLE 3: Different types of humus

Humate	$C_{HA}:C_{FA} > 2$
Fulvate-humate	$C_{HA}:C_{FA} = 1-2$
Humate-fulvate	$C_{HA}:C_{FA} = 0.5-1$
Fulvate	$C_{HA}:C_{FA} < 0.5$

carbon dynamics in specific humic fractions, it has remained almost less explored.

Trace metals in wetland sediment

Trace metals vary widely in natural systems (soil/sediment, water and air) depending on their source. The trace element content of a soil is dependent almost entirely on that of the rocks from which the parent material was derived and on the processes of weathering, both geochemical and pedochemical, to which the soil-forming materials have been subjected. In the case sediment the above factors in conjunction with the medium of transportation and the medium of deposition also have high role. The more mature and older the soil, the less may be the influence of the parent rock^[43]. Similar is the case with sediment as well. The effects of human interference are generally of secondary importance. However, considering the tune of pollutants entering the environment in unit time, anthropogenic activities^[25,44-56] have significant contribution towards increasing concentration of trace metals. Pagnanelli et al.^[57] list out five different means of anthropogenic sources of metals into the environment and states that their fate is decided accordingly. The different types according to Pagnanelli et al.^[57] are (i) Dissolved form in the soil aqueous phase, (ii) In exchange sites on inorganic soil constituents, (iii) Adsorbed on inorganic soil constituents, (iv) Associated with insoluble soil organic matter, and (v) Precipitated as pure or mixed solids.

The condition of the atmosphere in most of the places in the world is becoming worse due to varieties of air pollutants from vehicular emissions and industrial processes such as metal refining and fossil fuel combustion^[58-66]. The atmosphere is now a significant transport medium for many trace metals (via wet and dry deposition) to ecosystems in and around urbanized as well as industrial areas^[67-70], also confirmed by historical deposition levels

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(geochronology) of metals in some areas^[71-72]. One of the common ways of treating industrial as well as domestic wastewater is the disposal on land (sewage irrigation), which has the greatest drawback of the possibility of heavy metal contamination. In many cities, the areas, where municipal wastewater is disposed, are showing elevated levels of trace metals in higher trophic levels of the food chain (Bioconcentration^[46-47,73]).

Trace metal concentration, distribution and migration in aquatic sediments

Lake, estuarine and coastal sediments and adjoining marshes act as ultimate depositories for heavy metals^[74-76]. Their elevated levels in the sediments can often be attributed to anthropogenic influences, rather than to geogenic means. Hence vertical distribution profiles of heavy metals in sediment cores may reflect the geochemical history of a given region, including changes due to anthropogenic impact assuming minimal post-depositional movement of metals^[77]. Studies related to the trace metal concentrations in estuarine sediments^[74], surface water and stream sediments^[78-80], soils around industrial belt^[81], soils in natural forests^[82] and even peat bogs^[83] report about the natural as well as anthropogenic inputs of trace metals, which are site specific according to the type and source of input. Mostly in urban wetlands, the inputs are from anthropogenic sources, like the atmospheric fallout as a result of burning of fossil fuels and the discharge of industrial as well as domestic sewage. Even the concentration of metal elements in sediments as well as in water in different wetlands in a same locality varies^[84] as a result of difference in the quality of wastewater entering the wetland and the type of utilization, i.e., for fishing and/or dumping of municipal solid waste and other incoming nonpoint effluents^[78].

Sediments play a major role in the pollution scheme of aquatic systems by heavy metals. They act as sinks and possible sources of pollution. Heavy metals are not fully permanently fixed in sediment particulates and can be released back to water column by changes in environmental conditions. The distribution of metals in the aquatic sediment may

provide a record of the spatial and temporal history of pollution in a particular region or ecosystem, although their concentrations are controlled by a variety of physico-chemical factors^[85], which in turn depend upon the parent materials^[86] and weathering processes^[87], hydrological and geochemical factors^[88-89], the climatic condition (seasonal variation). Aquatic sediments can accumulate a significant quantity of metals due to the metals' migration in anoxic ground waters^[90]. In aquatic sediments (large wetlands, lakes and ocean), there seems to be a pronounced seasonal variability between the dry and the wet seasons in concentration of trace metals as the concentration of sediment bound trace metals as well as their mobility at sediment-water interface is decided by the seasonal water circulation in such aquatic bodies. Seasonally anoxic lakes offer a range of redox conditions, which show spatial and temporal variations^[91].

Factors controlling metal(bio) availability, distribution and mobility

Total concentration, distribution, reactivity and mobility of trace metals in sediments are a function of organic matter, mineral contents, textural qualities of the sediments, and biogeochemical status of the aquatic system in question^[89,92-95]. Trace metals in aquatic systems have a range of forms starting from free metal ion to complexed and particulate form. The fate of the metal element within these three forms are determined by a number of environmental factors such as pH, redox potential^[96-97], ionic strength, anthropogenic input, ligand availability (the type and concentration of organic and inorganic ligands) and the available surface area for adsorption, which relates to the grain size distribution^[85].

Metals from sediments can be remobilized back into the water column through resuspension^[98]. The resuspension of fine-grained metal-rich sediments may influence the adsorption of metals on the particulate phase. In addition, early diagenetic degradations may also play an important role in the redistribution of metals^[99]. Textural heterogeneity of sediments should be addressed while assessing the mobility of trace metals as the affinity of the metal elements with different grain size (clay, silt and sand)

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decides the fate and the uptake by plants and other organisms. Muraleedharan and Ramachandran^[85] ascribes the fluctuation in trace metal concentration in the lower part of an estuary to the textural heterogeneity of sediments. Most of the trace metals precipitated on the fine particles because of the higher ratio between surface area and weight. These elements showed positive loadings with silt and clay content of the sediments and a greater affinity of these elements towards organic matter. The mineralogical composition of sediments also governs the spatial distribution of metals in the bottom sediments in aquatic systems. In general, the determining factors for the metal behaviour (e.g. mobility, bioavailability) can be classified as (i) Geochemical characteristics of a metal, (ii) Soil/sediment chemical equilibria, (iii) Mineralogical and textural properties of soil/sediment, (iv) Geological setting of the site, (v) Environmental variables including climatic factors, and (vi) Agricultural or soil management practices.

It is generally accepted that heavy metals are relatively immobile in most of the sediments^[100]. But the mobility and bioavailability of heavy metals in soils/sediments depends upon redistribution processes between solution and solid phases (mobility of metal elements from the surface water to the bottom sediment and vice versa) and among solid phase components^[101] as well as the change in the form of the metal elements (mobile λ immobile) which is regulated by a number of ambient conditions as already described in the previous sections (like pH, redox potential, ionic strength etc). The various controlling processes are largely responsible for the mobility and bioavailability of metal elements and hence the toxicity in aquatic systems may be listed as due to (1) Adsorption and desorption reactions^[88,102], (2) Solid-phase precipitation and dissolution reactions^[103], (3) Complexation-dissociation (Jorgensen & Jensen, 1984), and (4) Oxidation-reduction^[104-105].

Vertical distribution of trace metals in soil/sediment profile

The concentration of trace metals in soils or sediments varies from place to place depending upon a number of factors as discussed above. Even in the same geographical area, heavy metals show vertical

variations along a soil/sediment profile, i.e. different layers (horizons) of the soil column. The vertical variation could be due to the extent of atmospheric deposition^[106], ground water and other forms of contaminations, diagenetic processes and the underlying bedrock^[77], from which the soil profile has developed. Unless the underlying bedrock is a regular source of metals in a soil system, under natural ideal conditions, metal concentration should show a declining trend along the depth profile. But again, it depends on the content of organic matter and clay along the profile as trace metals have some affinity for these materials^[107]. The variation along a depth wise soil profile is also related with the textural properties in each of the horizons. Most of the studies show some sort of declining trend for metal elements along the soil or sediment profile, whichever the case may be, irrespective of habitat types, i.e. starting from a mineral soil in a forest^[108] to mangrove ecosystem^[95] and also a lake or ocean sediment^[77]. In each of these cases, the probable reason could be the association of trace metals with organic matter in the soil/sediment. However, issues such as precipitation of metal sulphides in anoxic conditions can also influence the situation.

Friedland et al.^[44] studied both the spatial as well as temporal patterns in the content of trace metals in the forest floor in the green mountains of Vermont. He observed a varied trend in the concentration of metal elements along the elevation gradient of the forest. Metal contents increased while soil organic matter content decreased in the forest floor at higher elevations indicating atmospheric deposition. Friedland et al.^[45] studied the vertical distribution of trace metals in a forest floor and observed that concentration and accumulation of trace metals are more in the Oe horizon and decreased along the profile. Moreover the study of Zolotareva^[109] and Friedland et al.^[110] are also important so far the deposition of heavy metals in the forest floor is concerned. These studies have put emphasis on the atmospheric deposition of trace metals and the influence of through fall and litter fall on the rate of deposition of heavy metals.

Concentration of metallic elements in soil solution as related to differential pH was studied by

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Igeo	Igeo-class	Designation of sediment quality
>5	6	Extremely contaminated
4-5	5	Strongly/extremely contaminated
3-4	4	Strongly/contaminated
2-3	3	Moderately/strongly contaminated
1-2	2	Moderately contaminated
0-1	1	Uncontaminated/moderately contaminated
0	0	Uncontaminated

Tyler and Olsson^[111]. They studied the concentration of metal elements in several distinct patterns of soil solution from an uncultivated cambisol in central scania, south sweden and observed a significant correlation between metal concentration and soil pH i.e. a positive correlation between trace metal concentration and soil pH for most elements present as anions and a negative correlation for cationic elements. Another study carried out by Herrick & Friedland^[112] reports about the variable relation of soil pH with trace metal concentration and distribution.

Similarly studies regarding the distribution pattern of trace metals in estuarine sediment^[85-86], in lake and ocean sediments^[77] and in mineral soils^[108] highlight the influence of all the above-mentioned factors on the concentration as well as the distribution of metals.

Transport of heavy metals in aquatic environments

Geochemical cycling of elements is receiving wide attention due to the need for understanding the pathways of pollutants in our present environment. River processes form a major link in the geochemical cycle. Estimates on the world river transport of metals to oceans(as oceans are the ultimate sinks) indicate that the bulk of the transport in the river takes place in the particulate form^[60].

As heavy metal pollution in aquatic systems is mostly of anthropogenic origin it is of primary importance to establish the natural level of these substances, i.e. the pre-civilization level. Fossil argillaceous sediment(average shale^[113]) is a worldwide standard that can be used in such situations. Being uncontaminated, it satisfies the basic requirements for most elements.

Vaithiyathan et al.^[60] have also used this average shale as a reference to trace the metal enrichment in cauvery river. A quantitative measure of the extent of pollution known as the Index of Geoaccumulation (I_{geo}), as introduced by Muller^[114], is calculated as per the following formula

$$I_{geo} = \log_2 (C_n / 1.5 B_n)$$

Where C_n is the measured concentration of the heavy metal 'n' in the <2 μ m fraction of the sediment, B_n is the geochemical value in fossil argillaceous sediments and 1.5 is the lithological correction factor. Prusty et al.^[49] suggest a contamination index based on local situation where in a comparable uncontaminated area is taken as a background.

On the basis of the numerical value of the index, at least seven igeo-classes can be established^[115].

Speciation of trace metals in wetland sediments

Speciation is a word borrowed from biological sciences and developed into an important concept in environmental analytical chemistry. The term expresses the importance of the specific chemical forms of an element in the system, although in the context of environmental analytical chemistry the term differs in its minutia among authors. The elemental speciation was studied and described by some of the pioneering researchers^[116-117] and defined as the determination of the individual physico-chemical(or geochemical) forms of that element, which together make up its total concentration in a sample. In the last decade speciation is more thoroughly and widely discussed in several conferences and recently the international union of pure and applied chemistry(IUPAC) as stated speciation to denote the distribution of an element amongst defined chemical species in a system^[118]. Primarily the concepts emphasise the essentiality of speciation measurements for the study of the toxicity of metals to aquatic organisms^[88], plants^[105] and detritivores^[119], which play a key role in the processing of detritus in the wetland and terrestrial systems and for the understanding of the trace-metal transport in rivers and estuaries^[120]. Use of total concentration of the metal element as a criterion to assess the potential effects of contamination implies that all forms of given metal have an equal impact on the

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environment and provides little consideration of its bioavailability or its interaction with sediments, suspended particulates or water.

Trace metals are non-biodegradable. When they enter the environment, their toxicity is controlled to a large extent by their physico-chemical form. The mobility, transport and partitioning of trace metallic and metalloid elements along an environmental gradient (air, water, soil and sediment) depend on the chemical form of an element or its speciation^[121]. The evaluation of potential risks and the toxicity of metals require an assessment of the proportion of the metals in different geochemical forms^[122-123]. Even a slight variation in the speciation of trace elements can dramatically change their bioavailability or toxicity. The word speciation not only refers to the chemical form of the element but also to the oxidation state, in which that element is introduced into the environment. The change of the oxidation state of an element can have a profound effect on its bioavailability and toxicity. For example: Chromium(III) is an essential element, whereas chromium(VI) is highly toxic^[124-125]. Pure tin has a low toxicity, while tributyl tin oxide is highly toxic^[126-127]. Arsenic(III) is much more toxic than arsenic(V)^[90,128-129]. Methyl mercury has more toxic potency than inorganic mercury^[130-131]. Therefore, to get information on the activity of specific elements in the environment it is necessary to determine not only the total content of the element but also its individual chemical and physical forms. The chemical partitioning of trace metals between different sediment forms is very important in determining the bioavailability and mobility of trace metals^[132-133]. Contamination in food products (e.g. oysters and mussels by organotin, fish by methyl mercury, and wine by lead compounds) is a prominent area that needs attention from the viewpoint of speciation.

As noted earlier major portions of toxic trace elements in aquatic systems are generally bound to particulate matter^[134], which eventually settles and becomes incorporated into sediments. Environmental conditions are important in controlling the metal speciation in the sediment. The most important controlling factors defining metal speciation at a particular point in space and time are pH, the

composition and the amount of organic matter and clay minerals, the presence and nature of Fe/Mn/Al oxides and hydroxides, the redox potential, the concentrations of salts and complexing agents (ligands), anion and cation content of the soil/sediment solution^[105,135-137]. The perturbation of the system (sampling, dredging, groundwater flow) impacts the measured speciation through one or more of these factors. However, some of the sediment-bound metals may remobilise and be released back to waters with a change of any of these above mentioned environmental conditions and impose adverse impacts on living organisms^[55,138-140].

Speciation analysis can be performed to identify at least five different types^[141] depending on the aim and scope of the analytical investigation: (1) Physical and chemical speciation {as for trace metal analysis of different forms in soil or sediment after sequential or parallel extraction}, (2) Screening speciation {as for determination of different methyl compounds, specifically methyl mercury, in tissue}, (3) Group speciation {as for determination of chemical compounds basing upon their oxidation states like Cr(III) and Cr(VI) or As(III) and As(V)}, (4) Distribution speciation {as for the determination of heavy metals in different parts/organs of an organism}, and (5) Individual speciation {as for the identification and determination of chemical species based on their molecular or electronic structure}.

The major changes in metal in sediments lead to the formation of five major metal geochemical forms^[149,116]: (1) Exchangeable fraction: loosely bound to the substrate and would change in concentration with changes in ionic composition of the overlying water; (2) Carbonate bound fraction: bound to detrital carbonates and changes in environmental pH would affect the binding of metals to carbonates; (3) Multiple hydroxide fraction: metals co precipitated with Fe and Mn oxides as coatings on particles, or as cements binding sediment particles together; (4) Oxidisable fraction: metals associated with organic matter can either be incorporated into tissues of living organisms, deposited as detritus or can be found as a coating over the grains. Metals associated with organic matter as well as sulphides would be released into the environment under oxidising conditions; and

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(5) Lithogenic fraction or residual fraction: the residual fraction of metal elements are those trapped in the crystal lattices of primary and secondary minerals, and only released to the environment upon complete destruction of the crystal in which they are found. Of all the five fractions heavy metals in the exchangeable fraction play a very important role in the evaluation of environmental condition and always act as pollution indicator^[142]. Metals bound to sulphides and organic matters are more stable and difficult to take part in the geochemical cycle and always act as a sink and reservoir for pollution. Metals in the residual fraction are safer to the environment for their lowest mobility and bioavailability.

The amount of a metal in any of the above-cited phase is dependent on the abundance of that particular phase in the sediment. The capacity of the pool to scavenge a particular metal element is known as scavenging capacity(SC), and to determine this, a phase normalisation with respect to its abundance is required. Hence the SC of a particular phase is determined by dividing the metal concentration of the pool by concentration of the major element(s) which make(s) up the phase^[49]. For example the SC of the carbonate phase of Cr is defined as:

$$SC = \left[\frac{\text{carbonate bound Cr in moles}}{\text{(Ca+Mg) of carbonate in moles}} \right] \times 100$$

A value of unity for the ratio would mean that, Cr would partition equally between the two pools given equal weight of (Ca+Mg) and (Fe+Mn). Values <1 indicate that reducible phase competes more effectively for Cr and the reverse is true with values >1. This approach of comparison of geochemical pools assumes that the competition between any pair of pools is not significantly affected by the presence of the third pool.

Various sequential extraction procedures have been proposed to assess the partitioning of sediment-associated metals amongst various geochemical phases and evaluate metal mobility and availability (for example^[116,120,143-144]). Even element specific methods have also been developed as that of Poulton and Canfield^[145] method for iron partitioning. However, the one proposed by Tessier et al.^[116] is widely used. The above indicated sequential

extraction schemes provide information about the extent of trace metal binding to the binding sites in sediments and help us in understanding their geochemical processes.

All the aforesaid metal fractions have a different mobility, biological availability and chemical behaviour. Thus it is necessary to identify and quantify the metal forms in order to assess the potential environmental impacts of contaminated sediments. Metals in soil solution; exchangeable metals and organically bound metals are considered as easily or potentially available and represent the most dangerous metal forms of the environment^[146-147]. Studies on the chemical speciation of aquatic sediments (rivers as well as lakes^[60,132-133,142,148-149], spring sediments^[150], soils from cultivated fields^[151-152], soils amended with sewage sludge^[73,153] as well as soils from polluted sites^[154] report about the differential affinity of trace metals towards these five above-mentioned phases. In most of the cases, the major geochemical phases for Cu and Zn are the residual and the organic phase, for Pb they are exchangeable and residual, for Ni it is residual, for Cd they are exchangeable, carbonate and residual, for Cr it is organic phase and for Fe and Mn they are residual and sometimes oxide phase. However, the affinity of the metals to a specific geochemical phase varies depending on the type of pollutant and water and sediment chemistry. It is clear that for most of the metals residual fraction is a major carrier or repository.

Trace metal-organic matter interaction in wetlands

The particulate trace metals in aquatic systems remain closely associated with the organic matter fraction of both water and sediment. To some extent there occurs a bonding between detritic(organic) matter and metal element resulting in a complex compound or salt of that particular metal element and it is not the fresh detritus, rather the organic matter fraction(i.e. humic fractions), which forms complexes with metal elements. When metal ions enter the environment and the living systems through natural or anthropogenic activities, only a small fraction will remain as free ion. The major chunk will be complexed with either inorganic or organic

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ligands. The stability of the complex varies from element to element. In addition to the organic matter fraction, sediments/soils have other inorganic and mineral fractions as well. Therefore, the binding mechanisms for heavy metals are complex and vary with the composition of the soil, the soil acidity and the redox conditions. Humic substances are strong organic ligands that form complexes with the metal elements, which vary according to the chemical behaviour of the metal element in question. Their binding intensity is affected by the metal species, the loading levels, the aging and the soil/sediment properties^[155] and also the behaviour of the organic matter^[156]. The metal binding capacity also varies depending on the vegetation type of the area^[157], as it influences the organic matter input.

Naturally occurring polyelectrolytes (complexing agents or complexants) referred to as HA and FA, ubiquitous in soil and natural waters, form both water-soluble and water-insoluble complexes with metal ions^[158-159] affecting their speciation as well as bioavailability to a large extent^[160-163]. Even the toxicity of a particular metal species towards aquatic organisms is probably related to the chemical form of the element (its speciation) as well as its ability to form complexes with the organic matter fractions, as the biological response (BR) of an organism is directly proportional to the activity of the free metal ion^[164]. Moreover the toxicity level is also dependent on the chemical nature of the complex (metal-humus)^[165]. Knowledge of this complexation of heavy metals with these heterogeneous macromolecules (humic and fulvic acids) is of great importance in determining their fate {metal(bio) availability and mobility in natural aquatic systems} in the environment^[166]. Depending on the type of ligand (the substance that complex with the metal ion), the group of metal ions can be subdivided as follows (Jorgensen & Jensen, 1984): (1) Simple aquated metal ions, such as $\text{Fe}(\text{H}_2\text{O})_6^{3+}$.

Metal ions complexed by inorganic anions, such as CuCl^+ and CuOH^+ . Metal ions complexed by organic ligands, such as amino acids, fulvic acid, humic acid and others, e.g., $\text{Cu}(\text{NH}_2\text{CH}_2\text{COO})_2$

Activity of metal ions at the binding sites

The chemical properties of the metals are one

of the most important deciding factors not only for the complexation with the organic matter fraction of soil, but also for the availability to aquatic organisms and for their activity at the cell surface binding sites. Microorganisms, including algae, synthesize extracellular ligands which complex metals and prevent their cellular uptake^[167]. Free metal ions are available, unless complexed with organic matter in the aquatic system, to act on the cell membrane, and the process involve the following steps^[168]:

Advection or diffusion of the metal in the bulk solution to the cell membrane surface; Sorption or surface complexation of the metal at binding sites on the cell membrane surface; and uptake (transport) of the metal through the cell membrane into the organism.

Therefore, a metal must first interact with, or traverse, the cell membrane surface to elicit a BR. The free metal ion activity, simply a measure of its chemical reactivity at the cell surface, determines the uptake, nutrition and toxicity of cationic trace metals. The free metal ion is believed to be in rapid equilibrium with cell surface binding sites^[169]. Certain metal species, however, are not able to react directly with cell surface binding sites, and thus, are considered biologically inactive. Such species include colloidal metals^[170] and those complexed to strong organic ligands^[171]. Studies on the aquatic chemistry of some toxic metals like Cd, Cu and Zn^[172] have indicated that the toxicity of these metals is due primarily to the presence of the free metal ion and thus may not be directly related to the total metal concentration. The metal binding sites cover a range of binding affinities to account for the heterogeneity of the humic material. Thus the selectivity of humic matter depends on the degree of loading, defined by the relationship between amount of metals and number of adsorption sites^[173].

Effect of organic complex formation on biological activity

Trace metals, though essential for the growth and metabolism of organisms, are also toxic above a certain concentration. Highly toxic elements include Ag^+ , Be^{2+} , Co^{2+} , Cu^{2+} , Hg^{2+} , Ni^{2+} , Pb^{2+} and Sn^{2+} , some of which may be lethal to some organisms (algae) at

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a lower concentration of $10^{-7}M$ and may interfere with metabolic functions. In the case of certain elements at lower concentrations deficiency symptoms are seen while at higher concentrations toxicity is experienced. Nutritional requirements also differ from organism to organism. The fungus *Aspergillus niger* for example increases its growth with Mo concentrations as low as $10^{-12}M$ ^[174]. The availability or addition of an organic complex forming substance in the growth medium may have the following consequences^[175]:

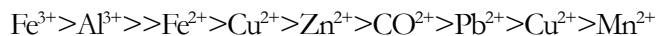
It may reduce the free metal ion concentrations in the solution, which may result in the increase or decrease in the growth of organisms (e.g, productivity). As a consequence of complex formation, the latter condition might result from the decrease in concentration of one or more essential micronutrients; the former condition might result because of the masking of one or more toxic elements.

It increases the total soluble metal concentration. Depending on whether the organisms can take up or breakdown the metal chelates, the metal species may become better available to the cells. Some chelates do not appear to penetrate cell walls and some other chelate formers may penetrate and may change the coordination chemistry of the inner portion of the cell.

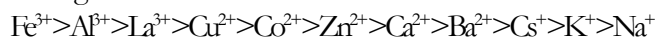
Humus-trace metal interaction in aquatic systems

Humic substances are ubiquitous in the aquatic environment and play important role in the mobilization/immobilization processes of trace metals and their toxicity. The affinity of metal elements with humus fractions is better understood by the knowledge of metal complexation capacity and conditional stability constants of metal-organic complexes. These are considered as physicochemical parameters for the roles of metal-organic complexes in natural waters and sediments^[176].

Humus compounds form salts and complex compounds with a variety of elements (with Al, Fe, Ca, Mg, Na, K and transition metals). Cations can be arranged in a series according to their capacity to form compounds with humus acids, which is known as the complexation capacity^[35].

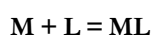


However, cations that form bridges (during the formation of mineral organic compounds), according to their influence on adsorbed humus acids, can be arranged as:



The position of metals in the series may change depending on the chemical nature of the humic substances, their origin and the pH of the medium in which the reaction takes place^[177]. The stability of the resultant organomineral compounds (Metal-ion/ligand complexes) is characterised by stability constants. The stability of humic acid complexes is in general agreement with the HSAB (Hard and soft acids and bases) principle^[178-180]: that hard acceptors prefer to bind hard donors and soft acceptors to bind soft donors and thus to form stable compounds. Confirming observations is documented by^[181]. The classification in brief is shown in TABLE 4.

In general terms, this reaction and the corresponding equilibrium constant are defined as follows^[182-186]:



$$K_{ML} = \frac{[ML]}{[M][L]}$$

Here M represents the metal ion, L the ligand, ML the metal-ligand complex and K_{ML} the stability constant, the square brackets denote concentration in appropriate units for aqueous solutions. Formal charges on M, L and ML are omitted for convenience. The larger the magnitude of the equilibrium constant K_{ML} the more stable is the complex ML in the solution. The interaction between the humus acid and the metal ion follows the above reaction.

If the humus acid denoted by the symbol HA-

TABLE 4: Elements classified according to HSAB system

Hard acceptor H ⁺ , Na ⁺ , K ⁺ , Be ²⁺ , Mg ²⁺ , Ca ²⁺ , Mn ²⁺ , Al ³⁺ , Cr ³⁺ , Co ³⁺ , Fe ³⁺ , As ³⁺	Intermediate Fe ²⁺ , Co ²⁺ , Ni ²⁺ , Cu ²⁺ , Zn ²⁺ , Pb ²⁺	Soft acceptor Cu ⁺ , Ag ⁺ , Au ⁺ , Ti ⁺ , Hg ²⁺ , Pd ²⁺ , Cd ²⁺ , Pt ²⁺ , Hg ²⁺ , CH ₃ Hg ⁺
Hard donor H ₂ O, OH ⁻ , F ⁻ , Cl ⁻ , PO ₄ ³⁻ , SO ₄ ²⁻ , CO ₃ ²⁻ , O ²⁻	Intermediate Br ⁻ , NO ₂ ⁻ , SO ₃ ²⁻	Soft donor SH ⁻ , S ²⁻ , RS ⁻ , CN ⁻ , SCN ⁻ , CO, R ₂ S, RSH, RS ⁻

Source: ^[178-180]

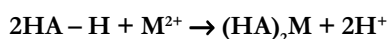
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TABLE 5: Properties of complexes of fulvic acids with some metals

Metal	K _{st}		Composition of the complex (number of moles of metal per mole of fulvic acid)
	pH 3.5	pH 5.0	
Cu	5.78	8.69	3.4
Pb	3.09	6.13	2.9
Fe(II)	5.06	5.77	2.1
Ni	3.47	4.14	1.6
Mn	1.47	2.78	1.5
Co	2.20	3.69	1.1
Zn	1.73	2.34	1.4
Ca	2.04	2.92	1.3
Mg	1.23	2.09	1.4
Fe (III)	-	-	6.1
Al	6.45	-	5.4

Source: [35]

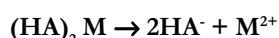
H(the H is given here for convenience of indicating in the equation given below) and the metal by M then the reaction with a bivalent cation M²⁺ can be written as:



The equilibrium constant K of this reaction is given by

$$K = \frac{[(\text{HA})_2\text{M}][\text{H}^+]^2}{[\text{M}^{2+}][\text{HA} - \text{H}]^2}$$

The stability constant of a metal humate can be written based on the following reaction:



Then

$$K_{\text{st}} = \frac{[(\text{HA})_2\text{M}]}{[\text{HA}^-]^2[\text{M}^{2+}]}$$

Similarly FAs also form complexes with metal elements. Some of the characteristics of the complexes of FAs with metals are given in TABLE 5[35]. The stability of these complexes varies with pH. At pH 3.5, the stability of the fulvic acid complexes are in the order of



However, the order is different at pH 5.0:



The nonintegral number of moles of metals per mole of FA as mentioned in TABLE 4 indicates the arbitrary nature of determination of molecular weights and the possibility of non-stoichiometric

TABLE 6: Logarithm of stability constant(log K_{st}) of compounds of humic acids with metals from ash soils

Cations	pH				
	3.0	5.0	7.0	9.0	11.0
Fe ³⁺	11.36	8.46	6.60	-	-
Cu ²⁺	6.79	12.60	12.33	-	-
Ni ²⁺	5.39	7.63	9.60	-	-
Fe ²⁺	5.36	6.41	4.78	-	-
Cd ²⁺	5.26	5.45	8.90	-	-
Zn ²⁺	5.05	7.15	10.34	-	-
Mn ²⁺	-	-	5.60	8.72	9.20
Ca ²⁺	-	-	6.45	7.81	8.03
Mg ²⁺	-	-	5.46	6.76	8.42

Source: [35]

ratios, partly due to the polydispersed nature of FA and the variable participation of unequal particles in organometallic interaction. For example, aluminium may be represented in different ratios by Al³⁺, Al(OH)²⁺.

The complexes of humic acids with metal cations are more stable than fulvic acid complexes. Among the above-mentioned cations, humates of Mn, Ca and Mg decompose totally in an acidic medium. The increase of pH upto a certain extent mostly increases the stability of the complexes(TABLE 6[35]). There is enough evidence[117] that clay particles coated with HA adsorb heavy metal ions and control their concentration in the system(soil/sediment/water). It may then be expected that the predominant form of the metal species in the soil solution or in the solid phase will be metal adsorbed on metal-humate colloidal particles.

The formation of complex compounds is of great importance in the transformation of mineral components of soils by increasing their mobility and migration capacity. The non-specific organic substances of the soil as well as humic fractions take part in these processes. In addition to these humic fractions other non-humic components of detrital matter also can bind and form complexes with metal elements. Extracts from plant litter are capable of holding considerable quantities of iron up to pH 9 to 10 in solution. Individual soil components are highly mobile and can be influenced by the complexation processes. All of these exert a destructive influence on the soil minerals and increase

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the availability of nutrients to plants; however, under unfavourable conditions it leads to the development of podzolization, a process of formation of an acidic unproductive soil called 'podzol', making most of the elements unavailable and a limiting factor for plant growth. The process of complexation has another significant influence, i.e. with the adequate amount of organic matter they bind the ions of many toxic metals such as Al, Cd, Ni and others, thereby decreasing the harmful effects of chemical contamination^[187-189]. Phenolic substances from plant residues entering the soil can actively extract Al, Mn and Fe from the soil. Salicylic, protocatechuic and phthalic acids are also equally capable for it.

Patrick. Jr. and Verloo^[96] reported the distribution pattern of soluble heavy metals (Fe, Mn and Zn) between ionic and complexed forms in saturated sediments, normally affected by pH and redox conditions. Fe, Mn and Zn differed in the extent of complexation with soluble organic matter. Approximately 60% of Fe and about 90% of Zn were found to be in a complexed form; whereas soluble Mn, on the other hand, was almost completely ionic under reducing conditions, i.e. the degree of complexation is very low.

Complexation capacity: definitions and measurements

Definition of complexation capacity

Heavy-metal ions are complexed by the organic matter in aquatic systems. This complexation of toxic heavy metal ions is of vital importance to the biota, because the 'complexing capacity' of metals determines their ability to render toxicity. In the case of pure ligands reacting with divalent or trivalent metal ions, although complexes of higher stoichiometry (1:2, 1:3, etc.) may form at low levels of metal, at higher levels 1:1 complexes predominate. The complexation capacity of the ligand is usually about 1 mole of metal per mole of ligand. The important point is that complexation capacity is a compositional parameter, rather than a thermodynamic one. For example the complexation capacity of the citrate ion (Cit^{3-}) is about 1 mole of metal per mole of citrate irrespective of pH, ionic strength, nature of the metal or the concentration

of the citrate ion used in the measurements. Theoretically, the complexation capacity (CC) of a humic substance or other complex mixture is a weighed average of the complexation capacities of the individual ligands in the mixture^[190]:

$$CC = \frac{\sum (CC)_i [\text{weight}]_i}{\sum [\text{weight}]_i}$$

Where $(CC)_i$ is the complexation capacity of the i th ligand in the mixture and $[\text{weight}]_i$ is a weighting factor that reflects the relative abundance of that ligand in the multiligand mixture. The nature of the weighting factor depends on the dimensional units of CC, commonly given in milliequivalents per gram. The complexation capacity of a humic substance varies considerably with almost every possible experimental variable i.e. pH, ionic strength, humic substance concentrations and the nature of the added metal ion^[190-191].

Measurement of complexation capacity

As the environmental chemistry of copper in water is better known, it can be used to model the general effects of other metals such as cadmium and zinc^[192-194]. The complexation capacity for other metals is also measured depending on the site-specific reasons, where other metals are the major sources of pollution. There are several methods in common use for measuring complexing capacity, and they may give quite different results. Therefore it is important, when quoting complexing capacities, to state the method used and to give all essential procedural details. Even variations in the same method (e.g., change in pH or electron rotation speed for ASV, i.e. anodic stripping voltammeter) can significantly affect the estimated complexing capacity value. Experimental studies can be conducted to examine metal complexation by humic substances at any pH, ionic strength, or combination of competing metal ions. However, quantitative modelling of metal-humic substance complexation has been carried out by single-metal complexation at constant pH and ionic strength^[190]. Even in such relatively simple systems, proper recognition of the effects of pH, ionic strength, nature of the metal, and the concentration of humic substance used in an experiment on metal-humic substance complexation

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is needed for interpretation of complexation capacity measurements and interpretation of thermodynamic data on metal-humic substance complexation. The extent of affinity between metal element and organic matter fraction (complexation capacity) is known in terms of the stability constants of the said compound. There are essentially two types of conditional stability constants. One is based on titration of ligands by metals (MT method), and the other is titration of metals by ligands (LT method). It appears that both procedures approach the end point of titration from opposing sides. Some differences are reported in the results obtained by MT and LT methods, both in the concentration of organic ligands reacting with metals and in the magnitude of the conditional stability constant^[195]. Although most of the complexometric titrations in case of soil and aquatic bodies are based on MT method, examination of the same with LT method and subsequently the variation between these two methods will be helpful to know the reaction kinetics in both the cases.

The method most frequently used for measuring complexing capacity is ASV titration^[116,196], where aliquots of a standard metal solution are added to the test solution, and the ASV peak height for the metal element is measured after a suitable equilibration method. Other methods used for determining complexing capacity are fluorescence spectroscopy^[159,162-163,197], electron paramagnetic resonance (EPR) spectroscopy^[198], differential pulse polarography (DPP), ion selective electrodes (ISE)^[199], potentiometric titration^[158,161,182,200] and chromatographic techniques^[201] also. However, many of these instrumental methods have their own technical limitations, for e.g. measurements through ISE and ASV. The estimation of stability constants using ISE is affected by inorganic ligand species in the medium that can render ionic copper unavailable to the ISE during the titration^[202]. The voltammetric method estimates unbound metal under operational voltages^[203]. Hence, the weak complexes, liable to become labile under the experimental conditions, may get excluded from the complexed form, which may subsequently lead to an underestimation of the complexation capacity and an overestimation of the stability constants as the constants estimated are due

to those complexes, which are stronger and non-labile ones under the operational conditions. Moreover, the analytical procedures involved may alter the original forms of the ligands. In view of these limitations, better realistic understanding of the dynamic situation is possible through advanced modelling of organic, natural and biotic, ligands, and metals together with analytical data. An array of computer based programs are available that can be used and the actual situation can be predicted. Some of the models that can be used efficiently for examining trace metal speciation are MINEQL/MICROQL, MINEQL+, MINTEQA2, COCSOC, CHESS and WHAM etc.

As the complexation capacity and stability constants vary from metal to metal, it is necessary to have extensive studies on the degree of complexation with organic matter on important toxic metals such as Cu, Ni, Mn, Fe, Cd, Pb. A review of literature shows that most complexation studies focus on seawater and marine system. Studies on fresh water systems and wetlands are comparatively less. Being more prone to human activities these systems need further attention. Wetlands and fresh water systems are also more linked with human life and sustenance especially in developing nations. They need to be conserved for the several ecosystem services they offer. Hence the necessity of extending these studies to wetlands as well as peat and marshy sediments level is high.

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER RESEARCH

It is noteworthy that wetlands have been called 'biological supermarkets' because of the extensive food chain and the rich biodiversity that they support. They trap nutrients and solids from intake water and help in its purification. The wastewater they receive has been the principle source of heavy metals in addition to the atmospheric fallout. Trace metals are well known for their bioavailability and their mobility along the sediment-water interface and the concentration of these elements increase in the different trophic levels in a food chain, known as bioconcentration/bioaccumulation. Thus the

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assessment of toxicity should be centered on the examination of the exact chemical form of the metal elements (pollutants) and their fate in the system rather than simply the total concentration. Moreover, the affinity of the metals with the organic matter influences the stability of a particular form of metal, in which it is supposed to be in the system based on the ambient conditions.

The dynamic nature of wetlands and the aforesaid tendencies of trace metals necessitate intensive studies regarding the speciation (different geochemical forms) of trace metals as well as their interaction with humic substances, the natural organic matter in the soil/sediment system. Moreover, it is further recommended that comparative studies on the complexation of metals with organic matter in different types of habitat (wetland, woodland and grassland) should be carried out simultaneously, which will give a complete understanding (comparative knowledge) of site specific processes and factors that influence the fate of metals in their repositories. Some of the key factors, which should be addressed, include:

- (1) Chemical and structural characterisation of humus
- (2) Identification of the mechanisms involved in complexation and other interaction between humic materials and metals
- (3) Examination of the interaction between the trace metals in the presence of both the humic fractions (HA and FA)
- (4) Comparison of the strength and stability of metal complexes between naturally extracted humic fractions with that of the reference standard, which is commercially available
- (5) Comparative study on the metal complexes with humic fractions derived from different types of humus
- (6) Implication of metal-humus interactions on metal dynamics in wetland systems and their impacts on biological systems.

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