

A REVIEW OF HEAVY METAL REMOVAL MECHANISMS IN WETLANDS

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ABSTRACT

Heavy metals are released into the environment from a wide range of natural and anthropogenic sources. The rate of influx of these heavy metals into the environment exceeds their removal by natural processes. Therefore there is attendance of heavy metals accumulating in the environment. Aquatic ecosystems are normally at the receiving end and usually, with wetlands as intermediaries. The conventional clean up technologies used in the prevention of heavy metal pollution are either inadequate or too expensive for some countries. In the past decades, therefore, research efforts has been directed towards wetlands as an alternative low cost means of removing heavy metals from domestic, commercial, mining and industrial discharge of wastewater. This paper is a comprehensive review of over 200 literature sources. It discusses the potential for heavy metal removal mechanisms by wetlands through reactions involving sedimentation, flocculation, absorption, co-precipitation, cation and anion exchange, complexation, precipitation, oxidation/reduction, microbiological activity and plant uptake.

INTRODUCTION

Increase of world population has resulted in the pollution of the environment. It is possible to summarize the main factors responsible for pollution and other types of environmental degradation in any community or society as being due to the combined effects of population increase, affluence and technology (Meadows, *et al.*, 1992).

Impact on the environment = Population × Affluence
× Technology

Man has set up complex treatment processes to prevent or control pollution from wastewater reaching the environment. The principle objective in wastewater treatment is to eliminate or reduce contaminants to levels that cause no adverse effects on humans or the receiving environment (Okia, 1993). A common method of removing heavy metals from wastewater has been to mix it with sewage, where conventional primary, secondary and tertiary treatment would then remove heavy metals. However, secondary and tertiary processes require high input of technology, energy and chemicals

(Tchnobanoglous, 1990). The costs of establishing and maintaining them with skilled personnel are also high. These treatment processes are therefore not very attractive or economically justifiable for large-scale smelting concerns or mining operations, especially in cash-strapped third world countries. A cheaper, but efficient treatment technology was therefore sought. Both natural and artificially constructed wetlands (so called passive technologies) offer such an alternative (Tam and Wong, 1994; Eger, 1994). Their increasing popularity over conventional treatment systems is justified by the advantages they offer, including low investment costs, low operating costs and no external energy input. They are more flexible and less susceptible to loading and they can be established at the site of production of heavy metals (Brix and Schierup, 1989). In addition they provide green space, wildlife habitats, recreational and educational areas. This review paper discusses the potential for heavy metal removal mechanisms by wetlands through reactions involving sedimentation, flocculation, absorption, co-precipitation, cation and anion exchange, complexation, precipitation, oxidation/reduction, microbiological activity and plant

uptake.

PURIFICATION CAPACITY OF WETLANDS

Observations show that both natural and artificial wetlands have a capacity to purify wastewater containing heavy metals (Matagi, 1993; Tam and Wong, 1994; Mbeiza, 1993; Denny *et al.*, 1995). The four main processes by which heavy metals are removed in wetlands are physical, chemical, biological and biochemical. These processes occur in the four main compartments of a wetland, i.e. (i) water (ii) biota (iii) substratum and (iv) suspended solids. The water compartment contains heterogeneous polyligands, i.e. fulvic, humic and tannic acids, amorphous metaloxyhydroxides of Mn, Fe, Al, clay, bacterial surfaces and associated exocopolymers, suspended particles and macro-molecules e.g. polysaccharides, proteins, etc (Greenland and Hayes, 1978; Tessier *et al* 1979; Luoma and Bryan, 1981). These substances demobilise the dissolved metal fraction of the incoming wastewater through various mechanisms. The water is effectively scavenged of heavy metals by precipitation of high molecular weight humic substances and hydrous oxides of manganese and iron, resulting in transfer of much of the dissolved heavy metals to the sediments due to adsorption processes which bind inorganic pollutants with varying strength to the surfaces by sediment colloids. In the biota, biological conversion occurs through assimilation and metabolism of micro-organisms living on and around the macrophyte and plant uptake and metabolism. In permanently anoxic water conditions in wetlands, decomposition of organic matter is by reduction and organic matter accumulates on the sediment surface. The resulting organic sediment surface is responsible for scavenging heavy metals from influent wastewater.

The physico-chemical forms for heavy metals once in the wetlands change dramatically depending on several characteristics of the metal and wetland. Emergent plants influence metal storage indirectly by modifying the substratum through oxygenation, buffering pH and adding organic matter (Dunbabin and Bowmer, 1992). The concentration of heavy metal ions removed from solution in wetlands is determined by interacting processes of sedimentation, adsorption, co-precipitation, cation exchange, complexation, microbial activity and plant uptake. It is, however, difficult to illustrate what actually occurs or which reactions take place in the wetland (Dunbabin and Browmer, 1992) because the processes are dependent on each other, thus making the whole process of heavy metal removal mechanisms in wetlands very complex. Nevertheless, the extent to which these reactions occur is determined by composition of the sediment especially by the amounts

and types of clay, minerals, hydrous oxides, organic matter, sediment pH, redox status and nature of contamination and plant genotype.

REMOVAL MECHANISMS OF HEAVY METALS IN WETLANDS

SEDIMENTATION AND FLOCCULATION

Once a heavy metal is in a wetland, whether the water is stagnant or mobile, a number of dynamic transformations may occur (Leewaugh, 1990 and Johnston, 1993). It may be transported from one compartment to another, e.g. from water to sediments or biota or suspended solids or vice versa. The process of sedimentation is closely related to the hydrological flow patterns of the wetlands. In calm waters particles which are denser than water will settle out. Sedimentation rates can be expressed in terms of vertical accretion (cm/year^{-1}) or mass accumulation ($\text{g/m}^3/\text{year}^{-1}$). Accretion rates reported for wetlands range from near zero for wetlands receiving little or no sediment to values greater than 1.5 cm/year^{-1} . However, accumulation rates exceeding $5000 \text{ g/m}^3/\text{year}^{-1}$ have been reported in floodplain wetlands and wetlands receiving agricultural run-off (Johnston, 1993). For particles, which are light or less dense than water, sedimentation become possible only after floc formation. Particles of clay and organic minerals which have surface electronic charge aggregate to form flocs, which generally settle more rapidly in a wetland than do individual particles (Hakanson and Jansson, 1983). Flocs may also adsorb other types of suspended particles including heavy metals. In wetlands, flocculation is enhanced by increased pH, turbulence, concentration of suspended matters, ionic strength and high algal concentration. Small particles flocculate more easily than larger ones in condition of high pH, low turbulence and high concentration and because of their larger surface area they have proportionally greater adsorption potential. Autochthonous production, resuspension and in the case of estuaries and brackish waters, salinity, are important facilitators in sedimentation and flocculation. The hydrous oxides of iron and aluminum carry a positive electrical charge necessary to neutralise the negative charges of colloidal particles resulting aggregation and sedimentation.

Sedimentation is not a simple straightforward physical reaction. Other processes like complexation, precipitation and co-precipitation have to occur first. Sedimentation is a physical process after other mechanisms aggregate heavy metals into particles large enough to sink. In this way heavy metals are removed from wastewater and trapped in the wetland sediments, thus protecting the ultimate receiving aquatic environment.

ADSORPTION

In sediments heavy metals are adsorbed to clay and organic matter by electrostatic attraction (Patrick *et al.*, 1990). Once adsorbed on to humic or clay colloids heavy metals will remain as metal atoms, unlike organic pollutants which will ultimately decompose. Their speciation may change with time as the organic molecules binding them decompose or as sediment conditions change. The extent to which metals ions are adsorbed by cation exchange or non-specific adsorption depends on many factors. These include properties of the metals concerned (valence, radius, degree of hydration and co-ordination with oxygen). Other factors are physico-chemical environment (pH and redox status), the nature of the adsorbent medium (permanent and pH-dependent charge complex-forming ligands), and the concentrations and properties of other metals and soluble ligands present (Alloway, 1992). For chemicals such as heavy metals more than 50% can easily be adsorbed onto particulate matter in the wetland and thus be removed from the water component by sedimentation (Muller, 1988).

The selectivity of clay minerals and hydrous oxide adsorbents in soils and sediments found in wetlands for divalent metals generally follows the order Pb>Cu>Zn>Ni>Cd, but some differences occur between minerals and with varying pH conditions. The selectivity order for peat has been shown to be Pb>Cu>Cd=Zn>Ca. In general however, Pb and Cu tend to be adsorbed most strongly and Zn and Cd are usually held more weakly, which implies that these latter metals are likely to be more labile and bioavailable (Alloway, 1990). It is usually found that adsorption of metal ions onto solids is described by either the Langmuir or the Freundlich adsorption isotherms equations. Metal adsorption onto manganese oxide can be described by the Langmuir equation for a range of metal concentrations, over about one order of magnitude only (Van den Berg, 1982). The isotherms do not provide any information about the adsorption mechanisms involved and both assume a uniform distribution of adsorption sites on the adsorbent and absence of any reactions between adsorbed ions (Alloway and Ayres, 1993).

Wetland plants translocate oxygen from the shoots to the root rhizomes through their internal gas space aerenchyma. The roots and rhizomes in turn leak the oxygen to the reduced environment. It is these oxidised conditions that promote precipitation of oxyhydroxides of Fe³⁺ and Mn²⁺. The precipitated hydroxides also act as absorption sites for other phytotoxic heavy metals present in the water compartment of the wetland (Wood, 1990).

CO-PRECIPITATION

Co-precipitation of heavy metals with secondary minerals, including the hydrous oxides of Fe, Al and Mn is an important adsorptive mechanism in wetland sediments. Cu, Mn, Mo, Ni, V and Zn are co-precipitated in Fe oxides and Co, Fe, Ni, Pb and Zn are co-precipitated in Mn oxides. Precipitation of Fe III is initially in the form of gelatinous stable forms, such as goethite. Ferrihydrite is more likely to be subsequently dissolved again through the decrease in E^h or pH than goethite. Ferrihydrite coprecipitates other ions and as a result of its large surface area acts as a scavenger sorbing both cations, such as heavy metals and anions, especially HPO₄²⁻ or H₂PO₄³⁻ and AsO₄³⁻.

Pyrite (FeS₂) forms in reducing conditions when sulphate become reduced to sulphide, producing H₂S which then reacts with Fe²⁺ to form FeS and FeS₂. The oxidation of sulphides such as pyrite causes marked acidification of wetland soils. This causes heavy metals to go back into solution. Specialised bacteria, e.g. *Thiobacillus ferroxidans* and *Metallogenium spp* are involved in the transformations of Fe and Mn respectively. Fe and Mn oxides occur as coatings on soil particles, fillings in voids and as concentric nodules. The oxide coatings are normally intimately mixed with clay and humus colloids and, although mineralogically distinct, form part of the clay-sized fraction.

The heavy metals normally found co-precipitated with secondary minerals in soil sediments are (Siposito, 1983):

Fe oxides: V, Mn, Ni, Cu, Zn, Mo
Mn Oxides: Fe, Co, Ni, Zn, Pb
Ca carbonates: V, Mo, Fe, Ni, Co, Cd
Clay minerals: V, Ni, Co, Cr, Zn, Gu, Pb, T, Mn, Fe

When reducing conditions cause the dissolution of hydrous Mn and Fe oxides, the concentrations of several other elements in the sediment solution are likely to increase. Cu, Co, Ni, Fe, V and Mn are generally more bioavailable from gleyed (periodically water logged soils) than from drained wetlands soils on the same parent material. However, Cu, B, Co, Mo and Zn do not undergo redox reactions themselves but are coprecipitated by hydrous oxides. Co-precipitation of heavy metals on carbonates (mainly CaCO₃) is very important in wetlands that drain limestone catchment areas. In chemisorption of Cd, where it replaces Ca in the calcite crystal.

PRECIPITATION

Precipitation is one of the major mechanisms by which

metals are removed from water in wetlands and deposited in the sediments. The formation of insoluble heavy metal precipitates is one of many factors limiting the bioavailability of heavy metals to many aquatic ecosystems. Precipitation depends on the solubility product K_{sp} of the metal species involved, pH of the wetland and concentration of metal ions and relevant anions. Precipitation from a saturated solution of a sparingly soluble heavy metal salt may be represented by the dynamic equilibrium $MX_2(s) \leftrightarrow M^{2+}(aq) + X_2(aq)$. The constant governing this equilibrium is $K_{sp} = [M^{2+}][X^-]^2$, i.e. at equilibrium the rate of removal of metal ions in the form of a precipitate equals the rate of their dissolution from the precipitate. When the values of the concentration of cation and anion are such that their product exceeds K_{sp} , precipitation occurs.

Under reducing conditions, carbonates, hydroxides and sulphides of metals are precipitated and their precipitation is also pH dependent. More specific for sulphides is that they are insoluble at neutral pH and therefore accumulate in fresh water wetland sediments. For the carbonates, the solubility is also influenced by partial pressure of CO_2 . For example the solubility of $PbCO_3$ can be increased several fold in the presence of CO_2 .

CATION AND ANION EXCHANGE

Ion exchange can occur between the counter ions balancing the surface charge on the sediment colloids and the ions in the wetland water. Negative charges on the sediment colloids are responsible for cation exchange, in which exchange of a hydrogen ion for the metal occurs. The extent to which the sediment constituents can act as cation exchangers is expressed as the cation exchange capacity (CEC), measured in $cmol_c/kg$. Sediment organic matter has a higher capacity than sediment colloids and plays a very important part in adsorption reactions in most soils even though it is normally present in much smaller amount (1-10%) than clays (80%). The negative charges on the surface of sediment colloids are of two types:

- (a) Permanent charges resulting from the isomorphous substitution of a clay mineral constituent by an ion with a lower valence.
- (b) The pH-dependent charges on the oxides of Fe, Al, Mn, Si and organic colloids which are positive at pH, below their iso-electric points and negative above their isoelectric points. Hydrous Fe and Al oxides have relatively high iso-electric points (>pH 8) and so tend to be positively charged under most conditions whereas clay and organic colloids are predominantly negatively

charged under alkaline conditions. With most colloids, increasing the soil pH, at least up to neutrality and tends to increase their CES. Humic polymers in the sediment organic matter fraction become negatively charged due to the dissociation of protons from carboxyl and phenolic groups. The concept of cation exchange implies that ions will be exchanged between the wetlands colloid surface (double diffuse layer) and the surrounding water. The relative replacing power of anion on the cation exchange complex will depend on its valence, its diameter in the hydrated form and the type and concentration of other ions present in water with the exception of H^+ , which behaves like a trivalent ion, the higher the valence, the greater the degree of adsorption. Ions with a larger hydrated radius have a lower replacing power than ions with smaller radii. For example K^+ and Na^+ have the same valence but K^+ will replace Na^+ owing to the greater hydrated size of the Na^+ ion.

The commonly quoted relative order of replaceability on the cation exchange complex of metals cations is $Li^+ = Na^+ > K^+ = NH_4^+ > Rb^+ > Cs^+ > Mg^{2+} > Ca^{2+} > Sr^{2+} = Ba^{2+} > La^{3+} = Al^{3+} > Tn^{4+}$

For individual sediment constituents, the order of replacement of the heavy metals is (Alloway, 1990):

Montmorillonite clay: $Ca > Pb > Cu > Mg > Cd > Zn$
 Ferrihydrite: $Pb > Cu > Zn > Ni > Cd > Co > SPMg$
 Peat: $Pb > Cu > Cd > Zn > Ca$

Anion exchange occurs when anions are attracted to positive charges on sediment colloids. Hydrous oxides of Fe and Al are usually positively charged and so tend to be the main sites for anion exchange in sediments. Most sediments have smaller capacities for anion exchange than cation exchange. Some anions such as NO_3^- and Cl^- are not adsorbed to any marked extent but others such as HPO_4^{2-} and $H_2PO_4^-$ are strongly adsorbed. Some organic pesticides, such as phenoxyalkanoic acid herbicides, exist as ions at normal sediment pHs and are adsorbed to a limited extent by hydrous oxides and by H_2 bonding to humic polymers.

COMPLEXATION

Complexation is a reaction whereby heavy metal ions replace one or more coordinated water molecules in the co-ordination sphere with other nucleophilic groups or ligands. Complexation reactions are important regulators of heavy metal ion speciation in water. In turn, speciation affects metal reactivity and toxicity (Brezonik, 1994). In the case of wetlands the ligands are mainly multidentate organic molecules. These are natural

organic matter, including humic, tannic and fulvic acids (HA, TA, & FA). An understanding of heavy metal organic interactions is therefore important in developing realistic models for heavy metal speciation in natural waters. The adsorption of cations on organic substances is mainly due to the general negative charge of these colloidal substances. Redox potential and pH are among some of the factors affecting this process. However the nature of HA and FA poses serious problems in this regard. They are polydispersed and chemically ill defined and this has resulted in a range of different models being advocated for the treatment of their interactions with heavy metals (Buffle, 1984).

Our ability to measure, represent and interpret the complexation equilibria of such vary from simple 'scatchard' model with 1:1 metal site stoichiometry and no site/site interactions to much more sophisticated 1:1 and 1:2 complexes, electrostatic site/site interactions plus explicit consideration of the nature of solution and complex phases.

Heterogeneous complexants exhibit at least three major distinguishing features.

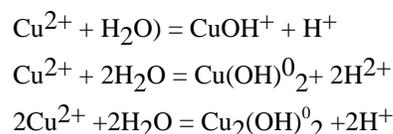
- (i) Their polyfunctionality, i.e. many complexing sites of different nature present on the same physical structure.

Their polyelectrolytic character (i.e. possible existence of high electric charge densities due to the presence of large numbers of dissociable functional groups per physical entity).

- (iii) The importance of conformational factors (e.g. reaction on surfaces, formation of aggregates etc.) The ability of dissolved organic matter to form complexes with ions in wetlands is of interest because of the associated biological implications, such as bioavailability and toxicity of heavy metals to living organisms and because of its relevance to efforts of understanding geochemical cycles of metals in the environment. The sequences of stability of complexes established by Jonasson (1977) is $\text{HgCu} > \text{Pb} > \text{Zn} > \text{Ni} > \text{Cu}$.

Bugenyi and Lutalo-Bosa (1990) showed that the highly alkaline organic and saline waters of the wetland-lake ecotone of lake George-Edward System in Western Uganda prevented heavy metal pollution from copper coming from a dormant copper mine at Kilembe and cobalt from stockpile tailings in Kasese. The major ions in the wetland-lake water are Na^+ , CO_3^{2-} and Cl^-

(Beadle, 1974) with high proportions of K^+ and Mg^{2+} (Melack and Kilham, 1972). Thus total dissolved solids, conductivity and salinity (three parameters that give a quantitative measure of ionic species in the water), water hardness (CaCO_3) and alkalinity are high. This relatively high concentration of ions increases the ionic strength of the water, a measure of electrical field in the water. The "chemical activity" is given by the product of the ionic concentration and the "activity coefficient". In water such as the above, the activity coefficients are less than 1 (it is 1 in the dilute waters) and hence the chemicals activities are lower than ionic concentration for any given ionic species (e.g. Cu^{2+}). That the activity of a species in the water is less than its concentration is interpreted as indicating that the species cannot act independently while it is under the influence of other ions in the water. Hence its effective concentration is decreased by the presence of other ions. Thus the wetlands-lake ecotone has sufficient dissolved ionic species to impart ionic interference to Cu^{2+} and thus reduce its effective concentration. The water has high concentrations of iron (Fe , 4.83 mg/l^{-1}) and organic matter (COD, 307 mg/l^{-1}). Boyle *et al.* (1977) and Sholkovitz (1978) demonstrated that copper reacts with iron oxide/organic colloids, which precipitate it as micro mole per kg concentrations. In the above water, iron oxide/hydroxide plays a significant role in the lowering of metal ions (e.g. Cu^{2+}) and effective concentration by precipitation on colloids and suspended particles. The pH range of the water is between 8-10. Within this alkaline range, the Cu^{2+} hydrolysis products include the following (Leckie and Davis, 1979):



The hydrolysis of Cu above further reduces its effective concentration. Copper is known to have great affinity for organisms, solid phases and organic matter (Bryan, 1971; Leckie *et al.*, 1979; Mantaura and Riley, 1975). The lake is eutrophied therefore with a lot of organic compounds, which reduces the chemical activity of the metallic ions through chelation, a particular form of complexation. It is the process whereby a single ligand containing two or more electron donor sites binds a single metal ion. This is the single most important factor in reducing copper toxicity (Hodson *et al.*, 1979). The cupric ions strongest bonds are with the intermediate electron donors (O, N, P) typical of dissolved organic matter (Kunkel and Manahan, 1973) and this complexation significantly effects the chemical and biochemical activity of copper.

OXIDATION/REDUCTION

The redox state of a heavy metal in solution is an important speciation parameter because it can drastically affect its toxicity, adsorptive behaviour and metal transport (Mertz and Cornazer, 1971; Henne *et al.*, 1971; Florence *et al.*, 1983). The redox state of the heavy metals depends on whether there are anoxic or oxic conditions in the wetlands. Micro-organisms, such as *Thiobacillus* spp catalyse the oxidation of sulphides. In the case of pollution by tailings from metalliferous mining, particles of ore minerals in the soils, such as, PbS, ZnS and CuFeS₂ become oxidised, releasing metal cations Pb²⁺, Cu²⁺, Zn²⁺ and Cd²⁺ into the sediment when they are adsorbed. Some organic pollutant molecules on the soil surface will undergo photolytic decomposition due to exposure to UV wavelengths in daylight and hence release the metal originally adsorbed on them. Oxidation of organic pollutants occurs by the action of oxygenase enzymes secreted by micro-organisms (Moffet and Zika 1987). Changes in redox potential E_n under reducing conditions allows the metals to precipitate as metal sulfides.

HEAVY METAL UPTAKE BY WETLANDS PLANTS AND MICRO-ORGANISMS

Mafabi (1995) defined wetlands as places where water stays long enough for plants and animals to become adapted to waterlogged conditions. In the case of wetlands plants, Denny (1987) recognised the following categories; emergent, surface floating, rooted leaves and submerged macrophytes. Denny (1980 and 1987) further noted that main route of heavy metal uptake in wetland plants was through the roots in the case of emergent and surface-floating plants, while euhydrophytes (plants that have completely submerged leaves or both floating and submerged leaves) take up heavy metals through leaves and roots. Denny (1980) further observed that the trend for greater dependence upon roots for heavy metal uptake was in rooted floating-leaved taxa with lesser dependence in submerged taxa. The tendency to use shoots as sites of heavy metal uptake instead of roots increases with progression towards submergence and simplicity of shoot structure. Submerged rooted plants have some potential for the extraction of metals from water as well as sediments, while rootless plants extracted metals rapidly only from water (Cowgill, 1974). In the case of foliar absorption of heavy metals, this is a passive movement in aqueous phase through cracks in the cuticle or through the stomata to the cell wall and then the plasmalemma (Price, 1977; Everard and Denny, 1985). In locating the sites of mineral uptake in plants, Arisz (1961) found that ions penetrated plants by passive process, mostly by exchange of cations. Winter (1961) demonstrated using rubidium ion movements that the

initial uptake was in Apparent Free Space (AFS), i.e. the volume of the tissue freely accessible to the diffuse of solutes (Briggs and Robertson, 1957). The apparent free space is composed of two fractions: Water Free Space (WFS) in which only water, molecules and free mobile ions are involved and the Donnan Free Space (DFS) in which mobile cations especially associated with the cell wall are distributed according to the Donnan equilibria (Brigs and Robertson, 1957). Winter (1961) confirmed that the uptake into AFS of *Vallisneria spiralis* L. leaves included both the WFS and DFS and concluded that cation exchange sites were located in the cell wall. The location of cation exchange sites in the cell wall was further confirmed by electron microscope studies of *Potamogeton pectinatus* leaf cells by Sharpe and Denny (1976). Frill *et al.* (1985) identified these sites and proposed the name phytochelatins. Phytochelatins are heavy metal complexing peptides composed of different amino acids (r- glutamic acid - cysteine)_n - glycine _n = 3 to 7, which are involved in detoxication and homeo-static balance of heavy metals in the plant cell. Excess heavy metals are bound to cell walls in a process called metathiolate formation through mercaptide complexes (Grill *et al.*, 1985).

Welsh and Denny (1979) demonstrated that lead was taken from the sediments into the submerged plants *Potamogeton crispes* L. and *Potamogeton pectinatus* L. by minimal translocation to leaf tips, dead regions and in lower older leaves, while extensive acropetal translocation for copper was observed in particular sites of accumulation. Electron micrographs of tissues of *P. pectinatus* showed that lead initially accumulated into cell by non-metabolic force flow of solute into the apparent free space (Briggs *et al.*, 1961; Welsh and Denny, 1980). It is then probably distributed according to the Donnan equilibria, associated with immobile anions such as pectates in both the cell wall and plasmalemma (Sharpe and Denny, 1976). In the moss *Grimmia doniana*, Brown and Bates (1972), reported that cell wall binding of lead was associated with anionic groups in the polyuronic acids. However (Sharpe and Denny, 1976; Welsh and Denny, 1980) concluded that the uptake of lead into *P. pectinatus* is a physical equilibrium with ionic or particulated lead binding to immobile sites in the cell wall free space and not necessarily associated with any specific exclusion mechanism. In contrast high copper concentrations were observed in active growing sites like stem apices and young leaves which acted as sinks for copper deposition. Further proof of copper translocation in plants is that copper is an essential trace element in photosynthesis especially in the photo system I and cytochrome biochemical processes (Golterman, 1975). Denny (1980) concluded that heavy metals were taken up by plants is by absorption and translocation and released by

excretion. Sharpe and Denny (1976) and Welsh (1978) showed, however, that much of the metal uptake by plant tissue is by absorption to anionic sites in the cell walls and the metals do not enter the living plant. This explains why wetland plants can have very high magnitudes of up to 200,000 times of heavy metal concentration in their tissues compared to their surrounding environments (Edroma, 1974; Oke and Juwarkar, 1996). This concurs with the results of Sutton and Blackburn, 1971 who demonstrated that under experimental conditions metals often accumulated in water plants to concentrations above those of the external media. *Myriophyllum spicatum* was shown to accumulate mercury when grown in sediments containing either organic or inorganic mercury compounds (Dolar et al, 1971).

The mechanism for metal uptake into shoots and leaves of submerged plants is summarised by Winter 1961:-

- (i) A passive penetration of ions (mostly exchange of cations) into the peripheral region the Apparent Free Space (AFS) i.e. the volume of the tissue freely accessible to the diffusing solutes which is made up of Water Free Space (WFS) and the Donnan Free Space (DFS).
- (ii) The active uptake of ions into the cytoplasm, the movements of different ions being independent.
- (iii) The active secretion of ions into the vacuole from the cytoplasm.
- (iv) The translocation of ions in the symplasm - an active process by which ions are transferred in the cytoplasm from cell to cell via the plasmodesmata.

Denny et al (1995) further proved that a natural papyrus wetland between Lake George, Uganda, and the river which brought heavy metals from cobalt tailings stockpiled as result of copper mining upstream at Kilembe mines prevented heavy metals from reaching the lake. This in turn prevented heavy metals from accumulating in the biota through the food web, thus protecting the fishery of the lake. The wetland's sediments, water and plants trapped the heavy metals. The heavy metals were trapped mostly by the roots of *Cyperus papyrus*, the dominant plant on the landward side of the lake. The roots of wetlands and plants are known to be efficient in waste water purification, hence the term root zone biotechnology. Further proof of heavy metal reduction in the rooted plants on the landward side of the lake has been supported by Mbeiza (1993) who found the following order of distribution root>rhizomes>stem>culm>leaves. However, plants in the highly metal exposed landward side of the lake were reduced substantially and sometimes killed due to

toxicity of heavy metals (Edroma, 1974; Mbeiza, 1993). Edroma (1974) further observed that in the contaminated areas high concentration of copper were found in the top soil and rapidly decreased with soil depth. He further observed that shallow rooted plants tended to have higher heavy metal concentrations than long deep-rooted plants and that very shallow rooted plants were often missing in the highly polluted soils. He observed that plants that grow near the heavy metal contaminated areas showed some degree of heavy metal tolerance. This tolerance is genetically determined and occurs through natural selection (Gregory and Bradshaw, 1965; Mc Neilly and Bradshaw, 1963).

Transfer coefficients (concentration of metal in dried portion of plant relative to total concentration in the soil) are a convenient way of quantifying the relative differences in bioavailability of metals to plants. Kloke et al (1984) gave generalised transfer coefficients for soils and plants. Sediment pH, organic matter content and plant genotype can, however, have marked effects on metal uptake. The transfer coefficients are based on root uptake of metals but it should be realised that plants can accumulate relative amounts of metals by foliar absorption of atmospheric deposits on plant leaves. Cd, Ti and Zn have the highest transfer coefficients which is a reflection of their relatively poor sorption in the sediments. In contrast metals such as Cu, Co, Cr, and Pd have low coefficients because they are usually strongly bound to sediment colloids. The discharge of heavy metals in wetlands may result in numerous physical, chemical and biological responses (Moore and Romanorty, 1984). Most responses depend upon physical and chemical characteristics of wetlands and the prevailing vegetation type. Macrophytes play a prominent role in nutrient and heavy metal recycling of many aquatic systems (Pip and Stepaniuk, 1992). While sediments form primary sinks for heavy metals, macrophytes may absorb heavy metals through roots and shoots. During the growing season, macrophytes communities can contain a substantial metal load which is released on senescence and death.

Some macrophytes can tolerate high concentration of several metals in their body mass without showing negative effects on the growth. Dunbabin & Bowmer (1992) found that macrophytes such as *Typha* and *Schenoplectus* are more tolerant than others. Although the mechanism of metal tolerance and uptake is poorly understood, it has been found that the whole process depends on sediment chemistry, i.e. pH, redox potential and organic matter. Temperature also is another regulating factor. In oxidised conditions 7 µg Cd/g⁻¹ reduced yields of *Oryza sativa* but under reduced conditions up to 320 µg Cd/g⁻¹ soil had no effect, reflecting the non-availability of the precipitated metal.

For uptake, therefore, oxidised conditions are preferable for efficient wastewater treatment by wetland systems.

Metal distribution in the plant tissue is of interest. *Typha* tolerates enhanced levels of metals in its tissue without serious physiological damage. Metal concentrations are reported to increase in the following order: roots>rhizomes>non green leaves>green leaves (Dunbabin & Bowmer, 1992). Under contaminated conditions, the greater proportion of metal taken up by plants was retained in the roots. The mean ratio of the metal loading in the roots was calculated and it was in order of magnitude Pb 77, Zn 29, Cd 12 and Cu 3. The green shoots have lowest concentrations of Cu, Zn, Pb and Cd.

Salati (1987) reported a study on heavy metal uptake by water hyacinth (*Eichhornia crassipes*) in Brazil. Water hyacinth is a plant with good tolerance and high uptake of nutrients and heavy metals, thus attention has been drawn to its heavy metal cleansing potential. The purification activity of water hyacinth is due to rapid growth in polluted waste water and the capacity to absorb heavy metals. After 6 weeks of growth in water containing heavy metals, the plant accumulated substantial concentrations of Cu, Pb, Cd, Hg and Cr (Wolverton and McDonald, 1976). The plant also reduces the Biological Oxygen Demand (BOD) of polluted waters. The efficiency is due to the absorption of the organic matter, fractionated and dissolved by the root "curtain" of the water hyacinth. These roots acts as filters through mechanical and biological activity, removing suspended particles from the water and thus decreasing turbidity. The reduction of turbidity by water hyacinth has been explained by the fact that the root hairs have electrical charges that attract opposite charges of colloidal particles such as suspended solids and cause them to adhere on the roots where they are slowly digested and assimilated by the plant and micro-organisms (Wolverton, 1989; Brix, 1993; Johnson, 1994). Zn and Cd are reported to be absorbed by *Cyperus esculentus* in oxidised sediments. Due to their abilities to absorb and tolerate heavy metals, several studies of plant metal content in relation to environmental metal concentration have been carried out with aquatic plants as pollution indicators (Pip & Stepaniuk, 1992).

Phytoplankton plays an important role in heavy metal dynamics in wetlands (Hammer and Bastian, 1989), e.g. zinc uptake by cyanobacteria decreased the concentration from 21 to 8 mg Zn/l¹ in a 15m area (Moore & Romanorty, 1984). Algae can concentrate Ur, Zn, Cu, Ni and Ra 226 in tissue in alkaline conditions (Hammer and Bastan, 1989).

Micro-organisms remove heavy metals directly from wetlands by two major mechanisms; the first is a metabolism dependent uptake of metals into their cells at low concentrations (some toxic metal ions are micronutrients for the micro-organism); the second is bio-sorption which is a non-active adsorption process binding metal ions to the extracellular charged materials or the cell walls. In micro-organisms, hydrophilic heavy metals ions are believed to be transported across the hydrophobic space of a biomembrane by the "shuttle" process of facilitated diffusion (or host-mediated transport) where a receptor molecule, e.g. a protein on the outer membrane surface binds a metal ion (Langton and Bryan, 1984; Boudon et al, 1983). The hydrophilic metal-receptor complex then diffuses to the interior of the membrane and releases the metal ion into the cytosol where it is trapped, perhaps by reaction with a thiol compound. The receptor then diffuses back to the other surface of the membrane where it may collect another metal ion. Alternatively, if the metal complex is lipid soluble, a much more rapid process of direct diffusion can take place. Direct diffusion differs from facilitated diffusion not only because it is faster, but because the ligand is also transported into the cytosol (Florence et al., 1983). Nature has provided aquatic fauna with effective defense against heavy metals which are eliminated via the gut or detoxified in the liver, kidney and spleen by a group of high sulphur proteins, the metallothioneins, which are synthesized in the organisms in response to heavy metal changes (Cross et al., 1978; Florence, 1983). These defenses allow them to cope with fairly high levels of heavy metals in the food chain and sediments. Toxicity occurs with spillover, i.e. when the metal uptake exceeds the body's ability to synthesize metallothionein. Evolution has not however equipped animals to tolerate free metal ions in water that contacts their gills or other exposed bio-membranes e.g. CuII ions bind initially to marine phytoplankton with a stability constant log b₁, in the range 10-12; complexing apparently occurring via protein and carboxylic acid groups (Florence et al., 1983). Cu is then transported across the biomembranes by a carrier protein (facilitated diffusion) where it reacts with a thiol (possible glutathione) in the cytosol or on the interior surface of the membrane and is reduced to CuI.

Heavy metals may therefore be removed from polluted wastewater in a wetland and retained in the sediments by plant uptake, micro-organisms associated with the surface of the roots and sediments, immobilisation via mechanisms such adsorption on ion exchange sites, chelation with organic matter, incorporation into lattice structures and precipitation into insoluble compounds.

CONCLUSION

UNEP (1984, 1992) estimated a combined total of 1150

million tonnes of heavy metals (Cu, Hg, Pb, Co, Zn, Cd, Cr) has been mined by man since the Stone Age. It further estimates an annual output of 14 million tonnes with an annual growth rate of 3.4% (UNEP, 1991). All this ends up in the environment. Wetlands help to prevent the spread of heavy metal contamination from land to the aquatic environment since there are usually at the ecotone (boundary between land and open surface waters). High metal removal rates of close to 100% have been reported both in natural and artificially constructed wetlands. The advantage of constructed wetlands being easy and cheap to construct and operate suggests they are a suitable alternative for wastewater purification. Although this paper has suggested removal mechanisms of heavy metal from wetlands, these have largely been extrapolated and correlated from other aquatic ecosystems such as lakes, rivers, estuaries, seas and oceans. A long term investigation with special emphasis on heavy metal removal mechanisms in wetlands is required.

The use of wetlands to control pollution is considered to be technologically, economically and environmentally acceptable, the retention of heavy metals in wetlands accumulates problems for the future. A wetland limits the spread of heavy metals, which are stored in the wetland instead. The destruction or harvesting of wetland biomass will release the heavy metals into the environment with the risk of the metals entering the food chain. The long term control of heavy metal pollution control, therefore, lies in the use of other technologies at the extraction, smelting and usage stages. The authors strongly recommend that environmental technology assessment (EnTA) should be used to address the global problem of environmental contamination from heavy metals.

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