

Water Technology Research Group

Trinity College, University of Dublin, Dublin 2 Ireland

ENVIRONMENTAL IMPACT OF ACID MINE DRAINAGE ON THE RIVER AVOCA: Metal Fluxes in Water and Sediment. Part I. Introduction to Metal Accumulation in Riverine Sediments

C. Herr and N.F. Gray



Water Technology Research
Technical Report: 19
Tigrone Press

Acknowledgements:

This work was funded by EU Contract: EV5V-CT93-0248 *Bio-rehabilitation of the acid mine drainage phenomenon by accelerated bioleaching of mine waste*

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First published March, 1995 (ISBN 1-872220-20-7)

This e-version: Published by Tigroney Press on behalf of the Water Technology Research Group, Trinity College, University of Dublin.

May, 2017

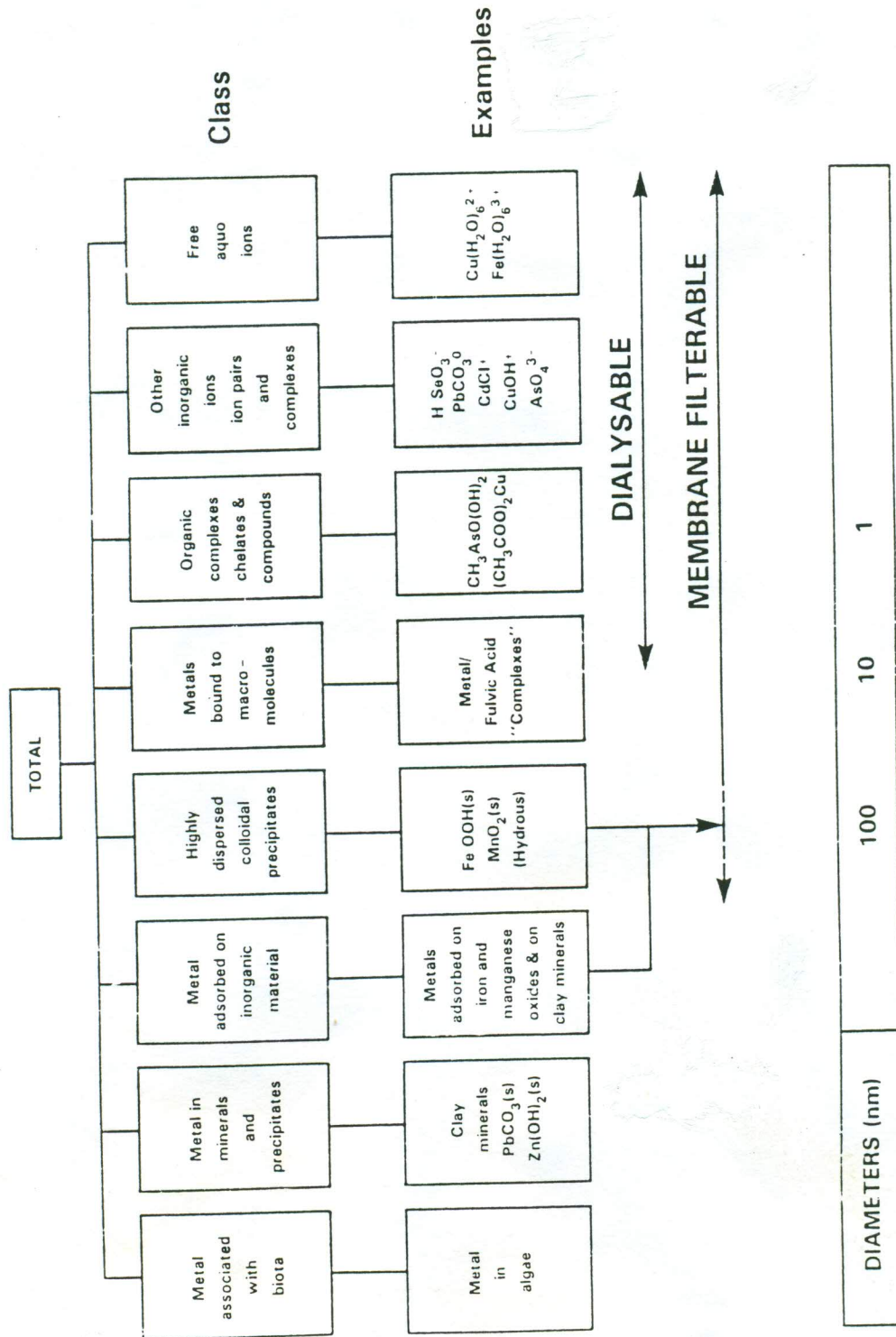
ISBN 978-1-912290-01-7

Generally more than 90 % of the heavy metal load in aquatic systems is bound to particles such as suspended matter and sediments (Calmano *et al.*, 1993), and more than 97 % of the total mass of transition metals is transported to the oceans by sediments (Gibbs, 1973). Natural particles in rivers, lakes and the sea consist of clay minerals, iron and manganese oxyhydroxides, carbonates, organic substances (e.g. humic acids), and biological materials (e.g. algae and bacteria) (Fergusson, 1990; Calmano *et al.*, 1993; Stumm, 1992). The composition of particles may be complex, involving both organic and inorganic coatings of particle substrate (Salomons and Förstner, 1984). The suspended matter and the deposited sediments are inter-linked through sedimentation processes. Thus, the capacity of particles to bind trace elements (e.g. ion exchange, adsorption) must be considered in addition to the effect of solute complex forms influencing the speciation of trace metals (Stumm, 1993). Processes taking place after deposition provide the interstitial (pore) water with potentially high concentrations of trace metals, which through processes such as diffusion (mixing of ions via natural thermal processes), consolidation (concentration and compression of particles) and bioturbation (remobilisation of metals caused by sediment feeding benthos) are able to influence the metal concentration of surface waters.

For any calculation involving chemical equilibrium, adsorption, or indeed toxicity, it is necessary to know the chemical form in which the element is present. Trace elements are present in natural waters in a wide variety of forms or species (Fig. 2). The truly dissolved species include free ions and both inorganic and organic complexes. Particulate species include metal associated with colloidal particles such as humic substances of high molecular weight and colloidal iron and manganese oxides. Metals are also associated with larger particles, such as clay minerals. The simplest distinction of metal species is between the 'filterable' and 'particulate' fraction. These are two operational terms which separate that part of a water sample retained by a filter and that which passes freely through a filter of usually 0.45 μm pore size (Kelly, 1988).

The speciation of a trace metal can influence its behaviour, fate and effects to a marked degree. In particular, the toxicity of trace elements to aquatic life can be greatly affected by the speciation. For example the

Fig. 2 Trace metal speciation in natural waters (French and Hunt, 1986).



complexation of Cu usually reduces the toxicity of the metal to a wide range of organisms (Hunt, 1986). French and Hunt (1986) in their investigation on species distribution in river systems found that up to pH 6 over 90 % of the dissolved Cu, Zn and Cd is attributed to free ions. The area of chemical speciation is fully reviewed by Morgan and Stumm (1991).

SORPTION PROCESS

Interaction with particulate matter

Interaction between particulate (e.g. suspended and bottom sediment, bacteria and algae) and metals play an important role in the regulation of dissolved metal concentrations. Adsorption and precipitation is the first step in the ultimate removal of trace metals from the hydrological cycle. Table 1 shows the important mechanisms and substrate types influencing metal binding and accumulation. Metals like Fe, Al, Mn, Cu, Zn are removed by attachment to particles, flocculation and sedimentation processes. Adsorption to solid phases, to biogenic particles and Fe-Mn hydrous oxides controls the concentration of a large number of trace metals in solution. Thus trace metals in natural waters are often lower than would be expected on basis of equilibrium solubility calculation or of water supply from various sources (Salomons and Förstner, 1984).

Processes most commonly encountered regarding binding of solutes onto sediments are adsorption, chemisorption and ion exchange. Physical adsorption on the external surface of particulate matter is based on van der Waals forces of the relatively weak ion-dipole or through dipole-dipole interactions. Chemical adsorption is characterised by the formation of chemical associations between ions or molecules from solution and surface particles. Sorption based on ion exchange is a chemical process in which negative or positive charges in the mineral lattice are compensated for ions possessing opposite charges (Salomons and Förstner, 1984).

Adsorption to surface areas is regulated by chemical parameters such as pH and salinity, concentration of metals in solution, and presence of complexing agents (e.g. dissolved organic matter) as well as type of

substrate (i.e. $\text{Fe}(\text{OH})_3$, Aluminium oxides and silica, organic matter) (Salomons and Förstner, 1984; Johnson, 1986). Adsorption can be quite system-specific, due to chemical variability among contaminants (adsorbants), aquatic particles (adsorbents) and the bulk solution phase. Furthermore the hydrological characteristics of the system of interest must be considered since the transport regime and bioavailability of adsorbed substances may be significantly altered by mechanisms involving settling and re-suspension (Young *et al.*, 1987).

Table 1. Estimation of the relative importance of mechanisms and substrates in metal accumulation (Salomons and Förstner, 1984).

	Detrital minerals, organic residues	Reactive organic matter	Trace metal precipitates e.g. oxides, carbonates	Iron and manganese oxy-hydroxides	Calcium carbonate, non-apatite phosphates
Incorporation in inert positions, eg., lattice-bound in crystals	XX			X	
adsorption=physical sorption	C	X		X	
Chemical sorption and co-precipitation	CC	XX	X	XXX	XX
Precipitation of discrete minerals			XXX		
Complexation/flocculation/aggregation	CC	XXX		CC	C

C, CC: Effective via coatings on other substrates

The role of hydrous oxides

The hydrous oxides of aluminium, iron and manganese play a dominant role in the transport of heavy metals in the aquatic environment. They occur as coatings around silicate grains and as discrete grains of oxide minerals. The hydrous iron oxide is often amorphous, although, of course well crystallised minerals occur in ancient sediment rocks (Drever, 1982). The ability of these oxides to interact with heavy metals has been known for years (Lee, 1975). Metal oxides exhibit ion exchange properties. In acid solutions the surface charge is positive and therefore the hydrous metal oxides act as anion exchangers, in basic solution, the surface charge is negative and act as cation exchangers. In neutral solutions the surface

charge is mixed, the particles show a limited capacity for exchange of both cations and anions (Stumm 1993; Schindler, 1991).

Hydrous oxides can arise from a variety of sources, including the weathering of various mineral species. In contact with oxygen containing water, reduced oxidation states of manganese(II) and iron(II) are oxidised to hydrous metal oxides. The presence of surface hydroxyls at oxide and hydroxide surfaces lead to the assumption that adsorption consists of complex formation of the adsorbed metal with the surface hydroxyls (Schindler, 1991).

A small shift in pH in surface waters causes a sharp increase in dissolved metal concentrations. The onset of adsorption is characteristic for each metal. Leckie *et al.*, (1980) showed in adsorption experiments of some metals onto amorphous Fe oxyhydroxide that the pH of adsorption increases in the order Pb<Cu<Zn<Cd<Ag. This means that under normal conditions in surface waters, lead and copper are more strongly bound to the surfaces of hydrous oxides than either zinc or cadmium. The hydrogen ion concentration is probably the most important factor influencing metal sorption. Heavy metal adsorption on oxide surfaces increases from near zero to 100 % over a narrow pH range of about two units (Fig. 3) which is different for each adsorbing ion, and to a lesser extent, different for each substrate (Drever, 1982; Salomons and Förstner, 1984; Sigg and Stumm, 1994).

SEDIMENTS

Sediments can reflect the current quality of the system as well as the historical development of certain hydrological and chemical parameters. The concentration of metals in the water column and the underlying sediment are related. Hence, any increase in trace metal concentration in the water column leads to a corresponding increase in the trace metal content of the sediment (Schindler, 1991). Clays in colloidal size ranges have an effect on the water quality out of all proportion to their concentration. Of the common pure clays - montmorillonite, illinite and kaolinite - montmorillonite have the greatest cation exchange capacity

(Thornton, 1983). Sediments are a sink or source for trace metals in the surface water. Metals are not necessarily fixed permanently by the sediment, but may be recycled via biological and chemical agents.

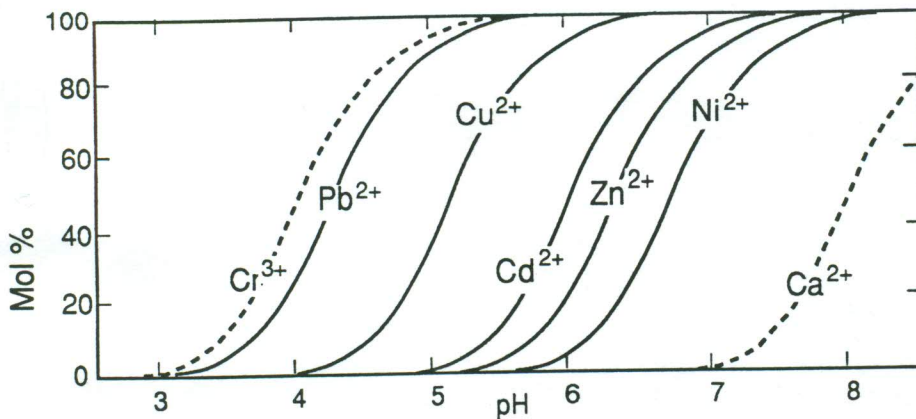


Fig. 3. Adsorption of cations onto oxide surfaces as a function of pH.

Sediment composition in river beds

All samples river bed material, in terms of their particle size distribution, fall into one of three categories - sand, gravel and mixed sand and gravel. Sand-bed channels are those where the distribution of the bed material is predominately finer than 2.0 mm in diameter, and gravel-bed channels have beds which are predominately composed of material greater than 2.0 mm (Gomez, 1987). Gravel river beds consist of a framework of coarse particles, with the interstices partially filled with finer sediments (termed the matrix) (Fig. 4). Two extreme gravel bed types are found, these are framework-supported (Fig. 4(a)) and matrix-supported gravel (Fig. 4(d)). The framework clasts are in tangential contact with one another and form a stable, self-supporting structure. In a framework supported gravel the volume that can be occupied by the matrix depends upon the packing arrangement of the framework clasts. In a matrix-supported gravel fine

material often exceeds 30 percent of the total load, so that large clasts are not necessarily in contact with each other (Church *et al.*, 1987). Particle size, factors relating to the mix of particles, surface texture and the temporal persistence of bed material are among the most critical physical aspects of mineral substrates. The substrate of a river bed is usually very heterogeneous, only in sandy bottoms of low gradient rivers is the substrate relatively uniform. Riffle-pool alteration, meandering and point bar development also contribute to small scale horizontal variation in substrate composition. No substrate is totally lacking organic material, however it consists primarily of inorganic matter (Allan, 1995).

In view of their chemical behaviour in nature, sediments can be divided into two distinctly different groups (i) fine sediments with particles smaller than about 63 μm , subdivided into silts and clays and (ii) coarse sediments with grains exceeding 63 μm , subdivided into sand and gravels. Fine sediments mainly consist of clay minerals, organic matter and fine grained quartz, carbonate and feldspar particles. Coarse sediments are generally less diverse consisting mainly of quartz with admixture of feldspar. Generally the coarse sediments consist of more or less rounded particles. The shape and size of the fine particles is diverse (Gordon *et al.*, 1992). Fine particles are charged depending on ionic strength of the surface water and type of surface coatings.

Grain size effects

Metals are not homogeneously distributed over the various grain size fractions, and large differences in total metal concentrations are observed in sediment samples from a single locality. Within the grain size spectrum the finer grained fraction which consist mainly of clay minerals show relatively high metal contents. In the silt and fine sand fractions the metal concentration generally decreases as fractions are dominated by coarse-grained quartz, feldspar and carbonate minerals with low metal contents. The reduction of grain size effects will reduce (not eliminate) the fraction of the sediment that is largely chemically inert (Salomons, 1993). The *chemical activity* of a sediment increases with decreasing grain size due to the increased specific surface area ($\text{m}^2 \text{g}^{-1}$) of fine clay particles. These fine particles therefore exhibit greatly increased levels of cation exchange

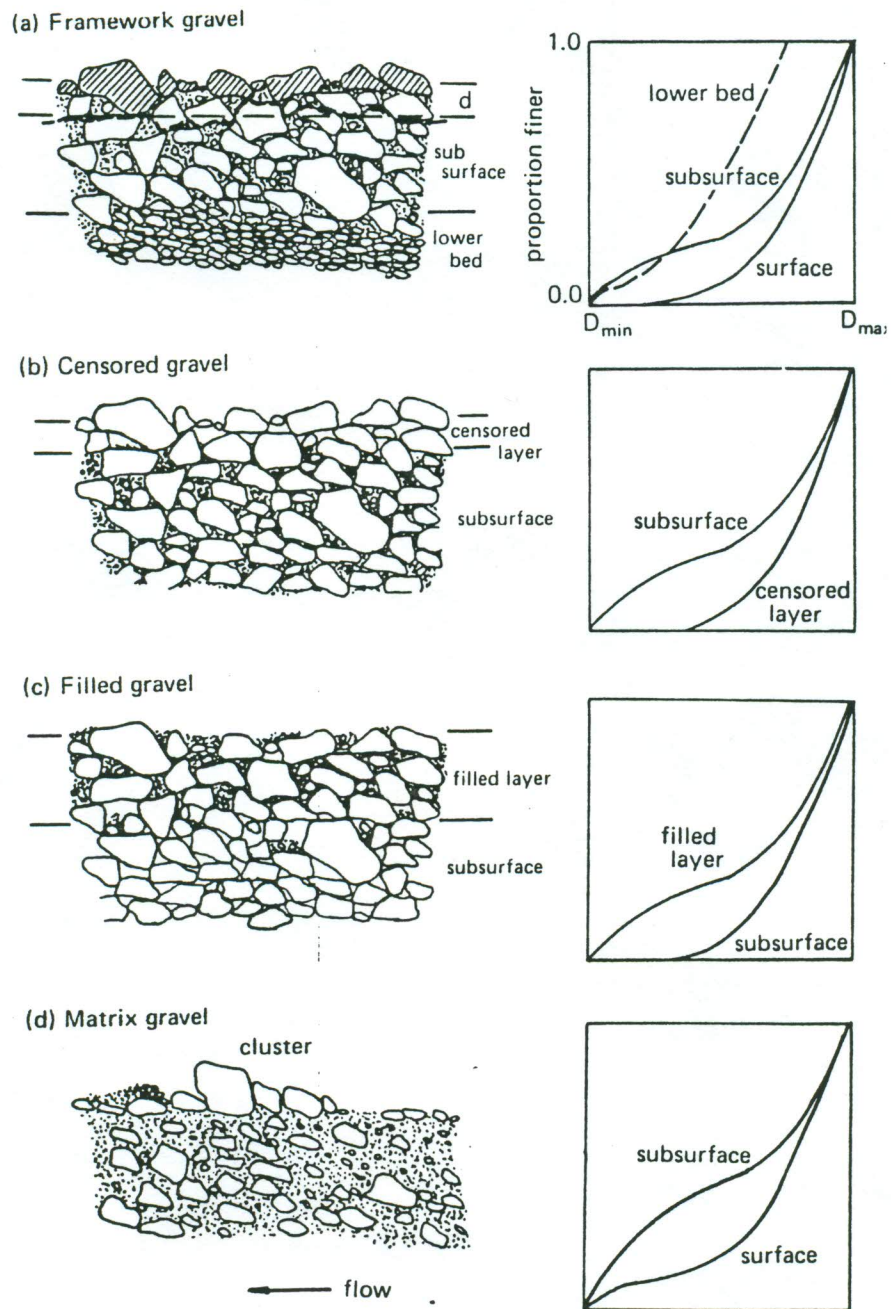


Fig. 4. Typical bedding for fluvial gravels. Type cumulative grain size curves on the right (D = grain size). In (a), d is the conceptual depth of the 'substrate'. The dashed line outlines a realizable 'surface volume' (Church *et al.*, 1987).

capacity (Webb and Walling, 1992). Manganese and iron hydrous oxides are exceedingly fine grained, with surface areas often on the order of $200 \text{ m}^2 \text{ g}^{-1}$ (Drever, 1982). As a result within a sedimentation area differences in pollutant concentration are observed, which are not related to differences in pollutant input but simply reflect the grain size composition of the particular sample analysed (Salomons, 1993). In the coarser fractions the heavy metals minerals may cause the metal portion to increase once more due to natural occurring mineral nuggets. Therefore it is of critical importance that all types of metal analysis in sediment should be based on a standardised particle size procedure. There is no general agreement on the particle size range to be separated from a sediment (Chester, 1988). However, Förstner and Salomons (1980) recommended the fraction $< 63 \mu\text{m}$ for metal determination for following reasons: (i) trace metals have been found to be mainly in clay/silt particles; (ii) this fraction is most nearly equivalent to the material carried in suspension (the most important transport mode of sediments by far); (iii) sieving does not alter metal concentrations - particularly when water from the same system is used; and finally (iv) numerous metal studies have been performed on the $<63 \mu\text{m}$ fraction, allowing better comparison of results

Transport and pollutant pathways

The transport of sediments is highly related to hydrological and geomorphologic phenomena. Sediment particles start moving when the flow of water exceeds a certain critical velocity. Similarly deposition occurs when these characteristics of the flow decrease below another critical value. Clay and silt sized components are the principal carriers of metals in sediments. Once the metal is associated with the solid phase it can be transported over long distances as long as the critical velocity of the river is high enough to keep it in suspension. As the flow regime of a river changes so the concentration of suspended metal will fluctuate (Webb and Walling, 1992). Mobility of sediments and their associated contaminants depend on hydraulic conditions which lead to a progressive sorting with respect to composition and size. The most significant sorting is in the coarse and fine sediments. The former are found in the more energetic areas such as steep rivers. Stream velocities of $0.05\text{-}0.06 \text{ m s}^{-1}$ have sufficient energy to resuspend clay, silt and particles from a stream bed and move them

downstream until the stream energy is expended and the particles settle out of suspension (Feltz, 1980). This is illustrated by the Hjulstrøm curve (Fig. 5).

The distribution and fate of a pollutant in the aquatic environment depends upon the nature and magnitude of the transporting processes and upon the biogeochemical transformation processes which may alter the geochemical compound (Ellis, 1986). Various physical processes with regard to distribution of pollutants in an aquatic system are dependent on the interaction of inflow, outflow and source transport processes. The supply of suspended sediment can increase during times of high discharge and erosion from the land surface and by the resuspension of particles that previously had settled to the bottom of the water body. Consequently, the total advective flux of the river, which is the product of discharge and concentration, typically increases at a faster rate than discharge (Webb and Walling, 1992). Particles can represent an important chemical flux, especially where low turbulence or flocculation promotes the settling process. The fate of many 'particle-reactive' chemicals in surface waters is to be sorbed onto suspended particles, which ultimately settle to the bottom of the water body (Hemond and Fechner, 1994).

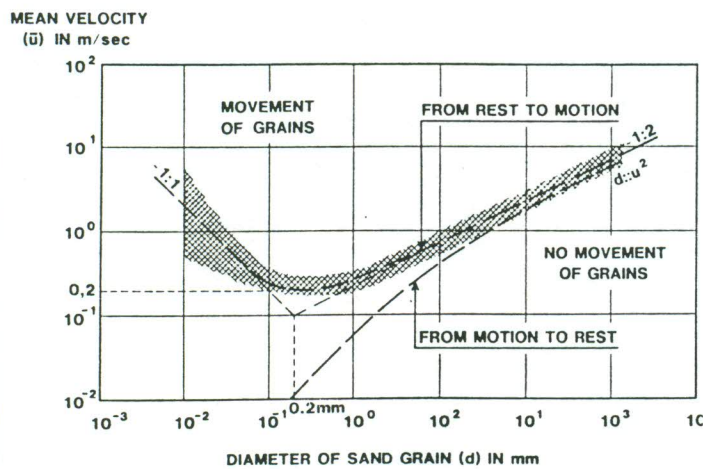


Fig. 5. The Hjulstrøm curve (Gordon *et al.*, 1992).

TOXICITY OF SEDIMENT-BOUND METALS TO AQUATIC ORGANISMS

An abundant and diverse community that include epipelagic microalgae, rooted aquatic plants, bacteria, detritivorous, filter feeding and predatory invertebrates, and bottom dwelling fish live in close association with the sediment-water interface (Campbell and Tessier, 1991). These benthic organisms may be confronted with an environment high in trace metal concentrations and as a consequence, trace metals will be accumulated in organisms. However, there is no straight forward relationship between trace metals concentrations in sediment and those organisms inhabiting the sediment (Campbell and Tessier, 1989). Hare *et al.*, (1994) working on Cd toxicity reported that the biological effects of contaminated sediment varied greatly between taxa, as determined by both an animal's sensitivity (direct toxicity) and the animal's behaviour (indirect toxicity) which results in significant alterations of the community structure of rivers. In North American streams contaminated with heavy metals, chironomids were found to be predominant in more heavily polluted waters, and caddis flies and mayflies in minimally stressed waters (Pesch *et al.*, 1995).

The toxicity of chemicals in sediments is strongly influenced by the extent to which the chemical binds to the sediment. The binding capacity of a sediment determines its trace metal availability. As a consequence different sediment types will exhibit different degrees of toxicity for the same total quantity of chemicals. Campbell and Tessier (1989) defined bioavailable metals *as metals in such a biologically available state that they can be taken up by an organism and can react with its metabolic machinery*. The bioavailability of metals in sediments appears to be altered by variations in sediment geochemistry (Luoma, 1989). High trace metal concentrations in sediments can be less harmful for organisms, whereas low concentration can be highly available and result in considerable accumulation. Sediments with high percentages of smaller grain size fractions (e.g. clay or silt), a high percentages of iron and manganese which can scavenge trace metals, or sediments with a high organic carbon content generally have a low availability of trace metals, irrespective of their load (Timmermans, 1991).

Di Toro *et al.* (1991) identified acid volatile sulphide (AVS) to influence the bioavailability of some sediment-associated divalent metals. Acid volatile sulphide, which is defined as the fraction of sulphides extracted by cold hydrochloric acid, consists primarily of iron monosulphides that are found in anoxic freshwater and marine sediments, and even in sands and gravels. It is suggested that when the concentration of AVS in sediments exceed that of divalent metals (Cd, Cu, Hg, Ni, Pb, Zn) sediments will not be acutely toxic. Iron in ferrous sulphide is replaced by dissolved metals and so they are removed from interstitial water by precipitation as metal sulphides. It was found that Cd and Ni concentration in worms generally increase with increases in sediment metal concentration, metal/AVS molar ratio, and metal concentration in interstitial water. However, the influence of AVS on divalent metals such as Cu, Zn, Pb and Hg in sediment, has not been thoroughly evaluated (Pesch *et al.*, 1995). Observations indicated that exposure of epibenthic and benthic invertebrates to different metals and non-ionic organics was correlated with concentration of these contaminants in the sediment interstitial water (Ankley, 1993). Additionally oxides of iron and manganese may also regulate the bioavailability of metals in oxidised sediments (Brook and Moore, 1988).

Bioaccumulation studies provide information on the bioavailability of toxicants, but give no measure of impact (i.e. stress induced reduction in growth), whereas while toxicant induced changes in energy budget parameters provide a sensitive and useful indicator of impact, they do not identify the casual cause (Rainbow and Dallinger, 1991). Zinc and Cu concentrations of invertebrates collected in unpolluted or moderately polluted ecosystems range between 75 and 200 $\mu\text{g g}^{-1}$ dry weight, respectively. In severely polluted ecosystems Cu concentrations were reported to be much higher (Timmermans, 1991). Species collected at the same location can exhibit different metal concentration in which various factors such as biomagnification, physiology and body weight play an important role. Primary producers, such as algae, absorb metals directly from the surrounding water, but organisms occupying higher trophic levels such as macroinvertebrates and fish, consume metals through the food web, in addition to direct uptake from their surroundings.

The Ontario Ministry of Environment and Energy (MOEE) identified *severe effect levels* for sediment quality guidelines as the level at which significant biological impacts are anticipated. These concentrations in bulk sediment for Cr, Cu, Pb and Zn were 111, 114, 250 and 800 $\mu\text{g g}^{-1}$, respectively (Krantzberg, 1994). However, total metal concentrations in sediment is a weak predictor of sediment toxicity and therefore limited in use for predicting site-specific environmental effects on organisms. This is due in large to the biotic and abiotic factors that influence metal bioavailability and consequently metal toxicity (Krantzberg, 1994).

Kemble *et al.*, (1993) identified a no-effect concentration (NEC) for Cu of 325 $\mu\text{g g}^{-1}$ (extracted with 3 N HCl) in sediments of the Clark Fork River, Montana. The no-effect concentration is the highest concentration of Cu in whole sediment that did not significantly reduce amphipod body length (28-d exposure). An effect concentration (ER-M) for total Cu is 390 $\mu\text{g g}^{-1}$ (Long and Morgan, 1991 cited in Kemble *et al.*, 1993). Exceeding an NEC (or an ER-M) for a particular chemical does not mean the chemical caused the effect. It is the concentration of a chemical associated with a response. However, if a sediment sample is toxic and the concentration of the chemical of interest is below the NEC, then the toxicity cannot be attributed solely to that chemical (Kemble *et al.*, 1993).

The discharge of water containing high concentrations of dissolved iron, for example as a result of mining operations, causes iron to precipitate as hydroxides and form ochreous deposits on the bed of the receiving water course. Ochreous deposits affect the stream environment in much the same way as other suspended solids but the effluents may have more serious direct consequences, if iron precipitates on the gills or other respiratory surfaces of fish or invertebrates. Continuous precipitation results in increased turbidity which may impair feeding ability of invertebrates through reduced vision or interfere with collecting mechanisms of filter feeders. Precipitation of iron deposits onto the leaves of macrophytes or the surface of algae, may inhibit photosynthesis and ultimately lead to the disappearance of the plants (Hellowell, 1986). Blanketing of substratum through deposition of material results in filling of interstices and can lead to substrate instability. Consequences are a

change in benthic community structure, the loss of species inhabiting interstices, reduction in species diversity and habitat loss.

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