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Chapter 5

TRACE METALS IN FRESH WATERS (WITH PARTICULAR REFERENCE TO MINE EFFLUENTS)

ULRICH FÖRSTNER

INTRODUCTION

Analyses of trace metals (concentrations less than 1000 μg/l; Wilson, 1976) were first performed in marine waters and on surface and subsurface waters in traditional mining areas. From the beginning, these data have been related to questions of biological productivity and possible adverse effects on aquatic biota, as well as to methodological aspects.

Stock and Cucuel (1934) determined the Hg-content in samples from the proximity of the island of Helgoland (North Sea) using a procedure of electrochemical deposition of Hg on a copper wire. The results obtained by this method (0.05 μg Hg/l) are in accordance with values of Gardner (1975), who found average Hg-concentrations ranging from 0.0112 μg/l in the Southern Hemisphere to 0.0335 μg/l in the Northern (the increase of the latter concentrations probably results from the atmospheric Hg-discharges from the large industrial complexes of the U.S.A., Europe, and Japan). Noddack and Noddack (1939) performed trace-element analyses on waters from the Skagerrak; Wattenberg (1943) measured the contents of Cu, Zn, and other trace metals in waters from the Atlantic. In the early 50's, seawater from various areas was analyzed, e.g., by Chow and Thompson (1951; Cu – U.S. West Coast), Black and Mitchell (1952; Cu, Pb – Scottish coast), Griel and Robinson (1952; Ti), Atkins (1953; Cu – English Channel), Lewis and Goldberg (1954; Fe), Emery et al. (1955; P), Morita (1955; Cu, Zn – coasts of Japan), Mullin and Riley (1956; Cd), Rona et al. (1956; U), and Sugawara et al. (1956; V).

Trace-metal analyses on continental waters were commenced in the U.S.A., in central Europe, the U.S.S.R. and Japan, mainly in areas where local anomalies from ore mineralizations had been expected. Huff (1948) studied the concentrations of Cu, Pb, and Zn in five samples from the Colorado River; Turekian and Kleinkopf (1956) analyzed the abundance of Cu, Mn, Pb, Ti, Ni, and Cr in surface waters of Maine. Investigations and literature compilations have been performed during the 60's and early 70's by Merrill et al. (1960; Be – Delaware and Hudson rivers), Durum and Haffty (1961), Livingstone (1963; surface waters), White et al. (1963; subsurface waters), Silvey (1967; California), Turekian et al. (1967; Neuse River, North Carolina), Bradford et al. (1968; Sierra Nevada), Voegell and King (1968; Mo – Colorado), Angino et al. (1969; lower Kansas River basin), Linstedt and Kruger (1969; V – Colorado), Weiler and Chawla (1969; Great Lakes), Durum et al. (1971; surface waters), Bradford (1971; California), Mills and Oglesby (1971; Cayuga Basin), Robbins et al. (1972; tributaries to Lake Michigan), Mathis and Cummings (1973; Illinois River), and Proctor et al. (1973; Missouri River). In central Europe early investigations have been performed by Heide and Singer (1954) and Heide et al. (1957) on the concentrations of Cu, Zn, and Pb in the Saale River (German Democratic Republic), by Heyl (1954) in the Siegerland mining area (Federal Republic of Germany), and by Fricke and Werner (1957) in mineral waters of Nordrhein-Westfalen (Federal Republic of Germany). Both the European and Asian surface waters of the U.S.S.R. have been studied intensively; compilations and original data are given by Konovalov (1959), Udodov and Parilov (1961), Kontorovich et al. (1963), Konovalov et al. (1967a, b), Konovalov and Ivanova (1972), and Konovalov and Nazarova (1975). An early review of data on acidic mine drainage – which is the central aspect of the present compilation – was given by Smirnow (1954). Of the early Japanese investigations on trace metals in natural waters one should particularly mention the studies performed at Nagoya University (Morita, 1955; Sugawara et al., 1956; Sugawara and Okabe, 1960; Kanamori and Sugawara, 1965).

During the last few years the number of trace-metal analyses has greatly increased in both geoexploration and environmental management. This progress has been partly due to improvement in analytical techniques which have significantly lowered the cost and increased the effectiveness of these methods. However, a critical review of many investigations clearly shows that the difficulties in the analysis of trace elements have not been fully overcome and that great care is still necessary to obtain valid data. Significant problems are still being encountered in respect to adequate sampling and storage procedures. Especially when taking water samples, contamination is often considerable due to unprotected sampling devices made of metal. It is assumed, therefore, that many of the earlier data on dissolved heavy-metal contents are too high. This is particularly true for the analysis of seawater, where – due to decisive breakthroughs in analytical and sampling techniques – metal values of one to two orders of magnitude lower than the data from the 60's and early 70's have recently been determined for Cd (Boyle et al., 1976; Martin et al., 1976; Bender and Gagner, 1976), for Cr (Cranston and Murray, 1978), for Cu (Boyle and Edmond, 1975; Moore and Burton, 1976; Boyle et al., 1977), Pb (Schaule and Patterson, 1978), Ni (Sclater et al., 1976), Se (Measures and Burton, 1978), and Zn (Bruland et al., 1978). Similar developments, even if not so spectacular, have been found or may be expected for freshwater analysis, particularly in less polluted waters, e.g., for parts of the Amazon River system (Boyle, 1978).

The present review does not claim to have discussed these questions in full detail. Its main purpose is to give an overview on the major sources of metals in surface waters leading to significant local or regional anomalies and particular problems arising from acidic effluents. Major aspects of actual interest include furthermore: transport phases of metal, dependencies on water discharge and biological productivity, background data, anthropogenic effects and the changes of trace metal concentrations at the river/sea interface.

SOURCES AND EFFECTS OF METALS IN NATURAL WATERS

In general, there are five sources of heavy metals in inland waters:

(1) Geological weathering. This is the source of “background levels”. It is to be expected that in areas characterized by metal-bearing formations, these metals will also occur in high levels in the water of the area.

(2) Industrial processing of ores and metals. During the processing of ores, metal-bearing dust particles are formed, which may be only partially filtered out by air-purification systems. Appreciable quantities of metals go to waste during chemical metal-refinement processes (e.g., galvanizing and pickling) by way of heavy-metal solutions, which are often discharged without any reclamation measures.

(3) The use of metals and metal compounds. Examples are the use of Cr-salts in tanneries, Cu-compounds as plant protection agents, and tetramethyl-Pb as an anti-knock agent. Examples of metal pollutants in industrial waste streams (sources “2” and “3”) are listed in Table I (from Barnhart, 1978).

(4) Heavy metals in animal and human excretions. Heavy metals are present in human and animal food – Zn in particular at relatively high concentrations. These metals are concentrated in excretions and mainly find their way to the water environment. The adult human excretes between 7 and 20 mg of Zn per day.

(5) Leaching of metals from garbage and solid-waste dumps. The contribution of

TABLE I

Some hazardous materials in industrial waste effluents (After Barnhart, 1978; with permission of the American Chemical Society)

Industry	As	Cd	Cr	Cu	Pb	Hg	Se	Zn
Mining and metallurgy	x	x	x	x	x	x	x	x
Paints and dyes		x	x	x	x	x	x	
Pesticides	x				x	x		x
Electrical and electronic				x	x	x	x	
Cleaning and duplicating	x		x	x	x		x	
Chemical manufacturing			x	x		x		
Explosives	x			x	x	x		
Rubber and plastics						x		x
Batteries		x			x	x		x
Pharmaceuticals	x					x		
Textiles			x	x				
Petroleum	x				x			
Pulp and paper						x		
Leather			x					

this source to the heavy-metal pollution of inland waters merits close attention. Mine dumps especially can be a serious source of pollution in connection with acidic solutions (see pp. 286–295). Acidity of surface waters imposes problems in all aspects of metal enrichment, ranging from the toxification of drinking water to problems concerning the growth and reproduction of aquatic organisms (Beamish and Harvey, 1972), the increased leaching of nutrients from the soil and the ensuing reduction in soil fertility (Whitby et al., 1976; Tamm, 1976), the increased availability and toxicity of metals with regard to essential plants (Lucas and Davis, 1961; Linnman et al., 1973) and finally to the undesirable acceleration of Hg-methylation in sediments (Fagerström and Jernelöv, 1972).

Viewed from the standpoint of *environmental hygiene*, metals may be classified according to three criteria: (a) non-critical, (b) toxic but very insoluble or very rare, and (c) very toxic and relatively accessible. Such a classification has been offered by Wood (1974) as given in Table II. Here, special importance must be attached to the non-metals As and Se aside from the heavy metals Hg, Cd, and Pb.

Water-quality criteria

Although it has been well-established that many inorganic constituents enter inland waters from natural or man-made sources, their significance with regard to surface water quality depends on many interdependent factors. Not only is the abundance and widespread occurrence of a particular constituent of importance, but also its availability in the form of solubilized species. For example, the toxicity of Cu is strongly reduced with the formation of Cu-organic complexes (Davey et al., 1974). Organic ligands, such as fulvic acids, NTA and EDTA, can inhibit the uptake of metals and thus may raise the toxic threshold (Sibley and Morgan, 1975; Andrew, 1976; Zitko, 1976; V.M. Brown, 1976). Experiments of G.A. Jackson and Morgan (1978) have shown that free-ion activity is a good indicator of Cu-toxicity to phytoplankton [1].

When setting permissible limits or ultimate goals for drinking-water standards, cognizance must be taken of the bioaccumulation via the food chain. Moreover, it is imperative not only to impose limits which protect man's health on the basis of trace-metal quantities in surface water from which potable water is extracted, but also to consider the environmental impact of these waters discharged to the environment. Such considerations involve the ecosystem as a whole, self-purification of river systems, biological-treatment plants, the effects of trace-metal enrichment on biological-purification treatment, the effects on crustaceans, fish, and ultimately on man. With regard to the different types of drinking-water contaminants, the trace metals have received considerable attention in terms of their toxic effects during the past few years. Unfortunately, it has to be admitted that many basic questions regarding this group of elements still remain unan-

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[1] These aspects are discussed, for example, in several papers of the symposium volume "Toxicity to Biota of Metal Forms in Natural Water", edited by R.W. Andrew, P.V. Hodson, and D.E. Konasewich, Int. Joint Commission Great Lakes Research, Windsor, Ontario (1976).

TABLE II

Classification of metals according to toxicity and availability (After Wood, 1974)

Non-critical			Toxic but very insoluble or very rare		Very toxic and relatively accessible		
Na	C	F	Ti	Ga	Be	As	Au
K	P	Li	Hf	La	Co	Se	Hg
Mg	Fe	Rb	Zr	Os	Ni	Te	Tl
Ca	S	Sr	W	Rh	Cu	Pd	Pb
H	Cl	Al	Nb	Ir	Zn	Ag	Sb
O	Br	Si	Ta	Ru	Sn	Cd	Bi
N			Re	Ba		Pt	

swered. As pointed out before, the question of chemical speciation poses one of the most difficult problems to be resolved by the chemist, pharmacologist, and toxicologist, especially regarding synergistic effects encountered in natural waters. Drinking-water standards have been proposed by various governmental bodies in accordance with toxicity data obtained from clinical investigations and various other studies, such as animal experiments. A brief summary is given in Table III compiled by Hattingh (1977), with additional data from the Federal Republic of Germany (Schöttler, 1977).

TRANSPORT PHASES OF HEAVY METALS IN RIVER WATER

In freshwater systems, the major difficulties in obtaining natural background data for trace metals arise from the great variability of rock formations, from the fluctuations in the water transport system (especially in rivers), and from the differentiation of particulate and dissolved metal species.

In particular two analytical techniques have been applied in *metal-ion speciation*: anodic stripping voltammetry (ASV) and ultrafiltration. The first procedure divides the metal species into two categories – electroactive (aqueous ions and "labile" complexes) and electroinactive (organic complexes and colloidal species). Ultrafiltration and dialysis is used to divide the metal species into different size fractions. The species that pass through the smallest pore size are generally taken to be free metal ions or small complexes.

A general schema of metal speciation – mainly based on the particle size fractions – has been given by Stumm and Bilinski (1972), and is reproduced in Table IV. In practice, the first step applied in separation of particulate from soluble metals involves filtration through a 0.45-μm pore-size membrane filter. The group of filtrable metal species can be subdivided into the following categories (Wilson, 1976):

(1) undissolved forms including colloidal and very finely divided materials;

(2) dissolved inorganic species, which, however, may exist in different oxidation

TABLE III

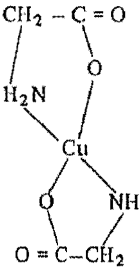
Drinking-water quality criteria (After Hattingh, 1977; Schöttler, 1977)

Parameter	USPHS (1962)	Japan (1968)	USSR (1970)	WHO European (1970)	WHO (1971)	SABS (1971)	NAS (1972)	Australia (1973)	EPA (1975)	FRG (1975)
As	10	50	50	50	50	50	100	50	50	40
Ba	1000	–	4000	1000	–	–	1000	1000	1000	–
Cd	10	–	10	10	10	50	10	10	10	6
Cr	50	50	100	50	–	50	50	50	50	50
Cu	1000	10 000	100	50	50	1000	1000	10 000	–	–
Pb	50	100	100	100	100	50	50	50	50	40
Hg	–	1	5	–	1	–	2	–	2	4
Se	10	–	1	10	10	–	10	10	10	8
Ag	50	–	–	–	–	–	–	50	50	
Zn	5000	100	1000	5000	5000	5000	5000	5000	–	2000

All values are in μg/l

TABLE IV

Metal species in aquatic systems (After Stumm and Bilinski, 1972; with permission of Pergamon Press)

Metal species	Range of diameters (μm)	Examples
Free aquated ions		$Fe(H_2O)_6^{3+}$; $Cu(H_2O)_6^{2+}$
Complex ionic entities		AsO_4^{3-}, UO_2^{2+}, VO_3^-
Inorganic ion-pairs and complexes		$CuOH^+$, $CuCO_3^0$, $Pb(CO_3)_2^{2-}$ $AgSH^0$, $CdCl^+$, $Zn(HO)^-$
Organic complexes, chelates and compounds	0.001 IN TRUE SOLUTION DIALYSABLE MEMBRANE FILTRABLE FILTRABLE	$Me-OOCR^{n+}$, HgR_2 
Metals bound to high-molecular-weight organic materials	0.01	Me-humic/fulvic acid Me-polymers
Highly dispersed colloids		FeOOH, Mn(IV) hydrous oxides
Metals sorbed on colloids	0.1	$Me \cdot aq^{n+}$, $Me_n(OH)_y$, $MeCO_3$, etc. on clays, FeOOH, organic
Precipitates, mineral particles, organic particles		$ZnSiO_3$, $CuCO_3$, CdS in FeS, PbS
Metals present in live biota	(Me = metal; R = alkyl)	Metals in algae

(3) dissolved metal-organic species, which can be subdivided into (3a) truly dissolved metal complexes and chelates, e.g. those with compounds such as amino acids, EDTA, and (3b) colloidally dispersed metal-organic associations.

As a practical example the distribution of Mn in the grain size spectrum in a sample from the Amazon River is reproduced in Fig. 1 (from Gibbs, 1977). The size separation for the various fractions to be analyzed was accomplished by centrifugation of the fractions >0.1 μm. For the finer solids and dissolved materials, a series of membranes of 300 Å, 100 Å, 30 Å, 10 Å, and 5 Å were used. An additional phase differentiation of the

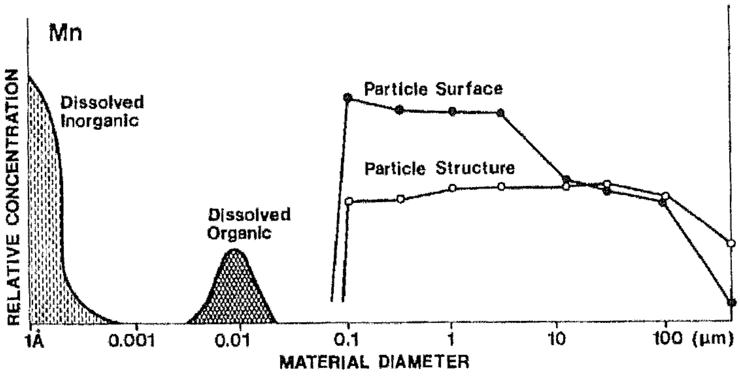


Fig. 1. Mn phases in the grain size spectrum of suspension samples from the Amazon River. (After Gibbs, 1977.)

solid particles – the procedures used are described below – indicates the decrease of the surface-bound metal content with increasing grain sizes, while the structurally bonded (more or less inertly incorporated) metal concentrations are fairly constant over the grain-size spectrum from 0.1 μm to 100 μm. The concentrations of both solid phases rapidly decrease to zero at approximately 0.1-μm particle diameter. The left-hand modes of dissolved organics (0.003–0.02 μm) and dissolved inorganic (<0.0008 μm) Mn-constituents are sufficiently small in particle size to assure physical transport of the material with the water mass. Conversely, the majority of right-hand Mn-modes (Fig. 1) are of sufficiently large particle size to be separated from the water mass.

The *source* of trace metals in aquatic systems significantly determines their distribution *ratio between the aqueous and solid phases.* For example, the bulk of the detrital trace-element particulates never leaves the solid phase from initial weathering to ultimate deposition. Similarly, metal dust particles (e.g., from smelters) and effluents containing heavy metals associated with inorganic and organic matter, undergo little or no change after being discharged into a river. This is attributable to the average residence times (in the order of days or weeks), which are too short for the establishment of stable, dynamic equilibrium between water and suspended material (Bowen, 1975).

Estimates on the world river transport of transition metals to oceans suggest that less than 3% is associated with dissolved species (Gibbs, 1977): Fe = 0.13%, Co = 0.3%, Ni = 0.5%, Cu = 1%, Cr = 2.5%, and Mn = 3%. It should be noted, however, that there are very large fluctuations even in the less-polluted systems. Gibbs (1977) gives the example of the Amazon River system, where the contributary Rio Negro carries very little sediment, so that almost the entire load of transition metals is transported in the dissolved-complexed phase. When the Rio Negro reaches the main channel of the Amazon River, the sediment-related metal transport surpasses the minor load carried in solution. Characteristic heavy-metal transport in less-polluted systems in a moderate climate (lower Mississippi River) is displayed in Table V by Trefry and Presley (1976). Only 11.1% (Cd)

TABLE V

Percentage particulate-associated metals of total metal discharge (solid and aqueous)

	Mississippi River [1]	Polluted U.S. rivers [2]	Polluted F.R.G. rivers [3]	Rhine River Netherlands [4]
Na	–	–	0.5	–
Ca	–	–	2.5	–
Sr	–	21	–	–
B	–	30	–	–
Cd	88.9	–	30	45
Zn	90.1	40	45	37
Cu	91.6	63	55	64
Hg	–	–	59	56
Cr	98.5	76	72	70
Pb	99.2	84	79	73
Al	–	98	98	–
Fe	99.9	98	98	–

[1] Trefry and Presley (1976); [2] Kopp and Kroner (1968); [3] Heinrichs (1975); [4] DeGroot et al. (1973).

to less than 0.02% (Fe) of the heavy-metal input to the Gulf of Mexico is transported in a dissolved-complexed state.

A similar sequence of the ratios between particulate and dissolved heavy-metal phases has also been found for polluted systems; typically, however, the dissolved discharges in polluted waters are significantly higher than in the less-polluted systems, particularly for metals such as Cd, Zn, and Cu.

In Table V, metal fractions in particulate form are indicated as percentages of the total metal discharges from U.S. rivers (Kopp and Kroner, 1968), rivers in West-Germany (Heinrichs, 1975) and from the Rhine River in the Netherlands (De Groot et al., 1973). The order of sequence of the mobility for a few selected metals is as follows: alkali and alkali-earth metals are predominantly present in a dissolved form; for trace metals such as B, Zn, and Cd the ratio of dissolved species to particulate species is between 2 : 1 and 1 : 1; Cu, Hg, Cr, and Pb exhibit ratios of the solid phases to the aqueous phases of between 2 : 1 and 4 : 1, whereas Fe and Al (and Mn under normal Eh conditions) are almost totally transported as solid particles.

DEPENDENCIES OF METAL TRANSPORT FROM WATER DISCHARGE AND ANNUAL CYCLES

The water discharge from river systems is one of the characteristic factors which can influence the ratio of metal concentrations in dissolved (filtrable) and solid (non-filtrable) species. Fig. 2 reproduces data given by Wilson (1976), which follows a graph by Hellmann (1970), for the development tendency of the non-filtrable and filtrable frac-

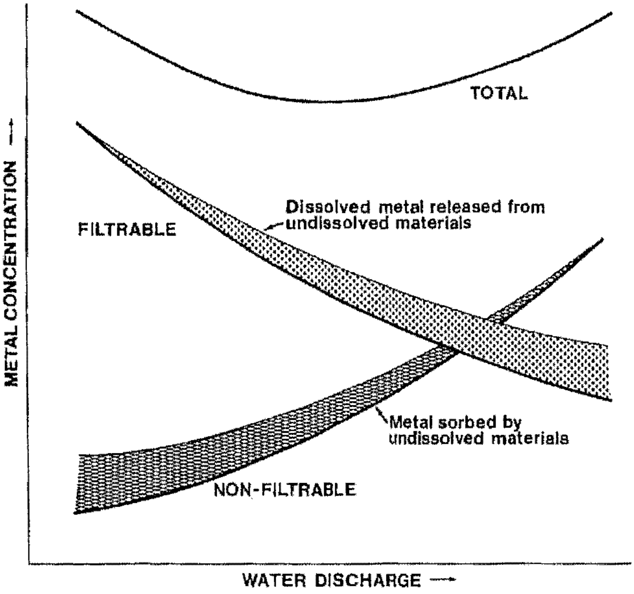


Fig. 2. Schematic presentation of the transport modes of trace metals in rivers. (After Hellmann, 1970, modified by Wilson, 1976.)

tions of the metal load with increasing water discharge. A decrease in the filtrable fraction is the result of dilution, whereas an increase of the non-filtrable fraction is mainly due to the resuspension ("flushing effect", see below) of particles from the river bed and its banks. The shaded areas of the upper section for both curves indicate minor effects of sorption, as in the case of the solid fraction, and remobilization from the particulates which increases the dissolved metal load to some extent. The decrease in the amount of sorbed cations with increasing discharge is due to (1) the higher percentage of relative coarse-grained material, which usually exhibits lower exchange capacities (see Chapter 4, pp.194–195); (2) a smaller amount of dissolved cations due to dilution; and (3) the shorter residence times of both solids and dissolved ions in the river channel, which in turn influence the attainment of equilibrium between both phases. However, metal cations are increasingly released from solid substances into the aqueous phase at higher water discharge rates owing to desorption and dissolution processes. There does not appear to be a significant variation in the total metal load with changing water discharges; the decrease of this curve for intermediate water flows in Fig. 2 should therefore be considered as being rather hypothetical.

Investigations into the dependency of trace-metal contents from water discharges was carried out, for example, on the Rhine River by Schleichert (1975). At the Koblenz sampling site on the middle section of the river, water samples were taken every working day between March 1973 and March 1974. In spite of considerable fluctuations, the following conclusions could be drawn concerning the metal contents of particulate matter of the highly polluted Rhine River system: (1) each discharge maximum can be ascribed to a concentration minimum, (2) the concentration changes of different trace elements occur more or less in the same form, and (3) extreme concentration peaks are rare, independent of discharge (these effects can be caused by short-term, local waste-water inputs as well as by remobilization of metals from deposits). Of the dissolved metal concentrations, only Cr showed this dependency, i.e., a decrease of metal content with increasing water discharge. Unfortunately, there is still no information regarding these phenomena from anthropogenically less-influenced systems. In this context, the findings of Aston and Thornton (1977) in their study of Cornish catchments are of interest, as they found a significantly smaller variation of heavy metals in both sediments and water of unmineralized areas than in the tributaries of the Carnon, Red and Gannel Rivers which are influenced by past and present mining and smelting industries.

Heavy-metal discharges in rivers may undergo characteristic developments in their *annual cycle*. From investigations on the temporal variability of metal transport by the Susquehanna River to the Chesapeake Bay, J.H. Carpenter et al. (1975) and Troup and Bricker (1975) found that the trace-metal concentrations correlate well with the amounts of solids discharged – the concentrations seemed to be highest in the spring and lowest in the summer and fall. This concurs with the findings of a major transport of heavy metals in associations with particulate matter mentioned above. Upon closer inspection, however, Mn, Ni, Zn, and Co exhibit large concentrations in January, and Cu, Cr, and Mn have concentration peaks in the late spring and early summer. When data are calculated for weight concentrations of metals in the solid fraction, it is found that all metals generally peak during December and January and secondary peaks occur for Co, Cr, Ni, Cu, and Mn in July. Since decaying organic matter is abundant in the Susquehanna River during these two periods, the high concentrations may be the result of metal bonding to such phases. Studies performed by Grimshaw et al. (1976) on the River Ystwyth in mid-Wales, where strong metal pollution from past mine operations is still obvious, indicate that metal concentrations in solution are highest during low flow periods, suggesting a dilution effect (which has been found by many other investigators, in particular from less polluted rivers, but also from polluted ones). For brief periods during the initial stages of storm runoff, there is a very significant increase of the metal concentrations in solution, apparently due to a flushing effect.

An important factor in controlling the trace metal content in natural waters is the ability of *planktonic material* to absorb some metals from solution. These effects have been thoroughly studied by Abdullah and Royle (1974a, b) in two surveys carried out on the Bristol Channel – where metal concentrations originate in runoff from mineralization zones and waste disposal – during April and June, 1971. The plot of the amount of acid extractable metal present in the suspended matter against the weight of solid in suspension (Fig. 3) shows a first-order relationship for Zn, Cd, and – approximately – for Cu during *April*. This uniformity suggests that the distribution of the particulates is con-

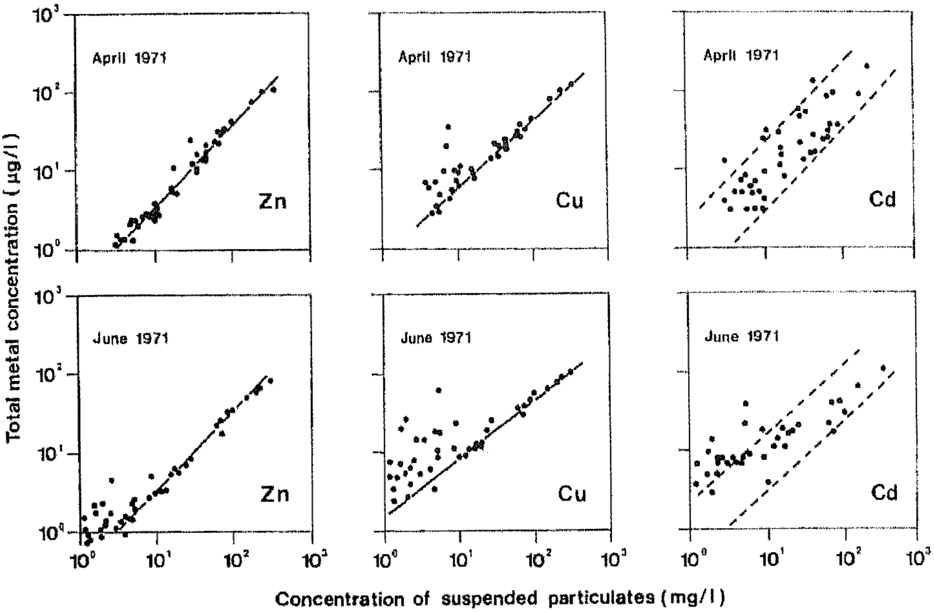


Fig. 3. Extractable metals in suspended matter from the Bristol Channel during April and June 1971. (After Abdullah and Royle, 1974a; with permission of Pergamon Press.)

trolled by mixing and turbulence and that little or no fractionation by settling takes place in the area studied. The positive anomalies found in the copper plot may be due to the contribution of particulate copper from north Devon and Cornwall runoff. For the *summer data* (June, 1971, below) Zn, Cu, and Cd plots show positive anomalies at stations situated in the outer part of the Channel, indicating that the additional metal is due to agencies other than runoff. The likelihood that plankton concentration of metal occurs, and not physical or chemical processes, may be deduced from the fact that the plot of the April data exhibits a linear relationship throughout the Channel (Abdullah and Royle, 1974a). Similar seasonal effects have been found by Knauer and Martin (1973) from studies on the uptake of Cu, Zn, Mn, Cd, and Pb by plankton in Monterey Bay, California.

Temporal variations in the metal distribution in three phases – biomass, allochthonous particulates and dissolved phase – were studied by Baccini (1976) from the Lake of the Four Cantons (Vierwaldstättersee). In the epilimnion the biogenic portion of the total particulate phase for Cu is approximately the same as the portion of the allochthonous phase and can even be higher during periods of high organic production. The distribution of Cu in the hypolimnion, however, indicates that the allochthonous portion dominates during periods of greatest sedimentation (May to September). These data show that Cu (and Zn) introduced in soluble form is transported into the particulate matter by plankton and that the Cu from decomposed sedimentary plankton is partially returned to solution, whereas the allochthonous particles are deposited on the lake bottom relatively unchanged.

DISSOLVED METAL CONCENTRATIONS IN LARGE FRESHWATER SYSTEMS

In order to determine the influence of both mineralization zones and civilizational effects, background values of metal concentrations are most desirable, which, although not "absolute", serve as *guidelines* in respect to major changes of the trace metal chemistry in inland waters (first column in Table VI). Most of these values stem from large inland waters, e.g., from the Amazon, Yukon, and Mississippi Rivers (2nd to 4th column). In these water bodies, civilizational effects are either still low or the inputs of contaminants are diluted by the large water mass.

The example of the *Amazon River* has shown that the various subsystems of large river systems may differ widely with respect to the concentrations of trace metals in both water and suspended matter. Irion and Förstner (1975) found in studies of Amazon "lake" sediments that deposits contributed by rivers from regions with heavily leached soils ("blackwater rivers", e.g., Rio Negro) are significantly depleted of Fe, Mn, Zn, Cu, and Co, when compared to the "whitewater" river deposits, e.g., from Rio Solimoes. Recent analyses of copper in the Amazon River system by Boyle (1978) indicate a similar distribution for dissolved metal species; the values of the black- or clear-water samples center around 0.5 μg/l, whereas the Cu-concentrations of the second group of rivers originating in the Andes, pre-Andes and southwestern Amazon lowlands, range between 1.5 and 2.0 μg/l.

For Gibbs (1977) it seems that in the Yukon River the content of metals such as Co, Cr, Cu, and Ni is slightly enriched in the dissolved phases, compared to the Amazon. This is probably due to lithogenic influences rather than civilization effects. The investigations on large rivers flowing through relatively unpolluted areas (Mississippi River) have shown that with improved sample extraction and storage and handling procedures, most of the data are significantly below those values which had been established as background data ten years ago (e.g., Turekian, 1969). However, there is still a good deal of controversy as to the origin of the sometimes strong divergences in the metal contents of inland waters, which are even greater than those for sea water. It seems that the amount of suspended matter, which can, on the one hand, partially pass through the filter (usually 0.45 μm pore size) and, on the other, can adsorb metals from solution, plays a considerably important role for the metal concentrations in water analyses. The Mississippi River, however, showed no significant seasonal changes in dissolved trace metals, although the suspended matter concentrations decrease from over 300 mg/l during periods of normal flow to 10 mg/l or less during the three month low flow period (Trefry and Presley, 1976).

The size of the water body also seems to be important in areas more strongly pol-

TABLE VI

Trace metals in freshwater systems (examples)
Values in $\mu g/l$

Metal	Background[1]	Amazon R.[2]	Yukon R.[2]	Mississippi[5]	L. Michigan[7]	Danube[9]	L. Constance[10]	Rhine[11]
As	1[7]	–	–	3[6]	1	1.5	3.7	13
Cd	0.07[3]	0.07[3]	–	0.1	0.3	<1	–	5.5
Co	0.05[2]	0.06[2]	0.1	–	0.2	<0.75	–	10
Cr	0.5[5]	2[2]	2.3	0.5	1.7	0.6	5.7	33
Cu	1[4]	1[4]	2	2	5	5	8.2	34
Hg	0.01	–	–	<0.1[6]	0.03	0.5	0.18	0.65
Ni	0.3[2]	0.27[2]	0.43	1.5	3	3	5	20
Pb	0.2[5]	–	–	0.2	1.5[8]	3	–	57
Se	0.1[7]	–	–	–	0.08	2.2	1.3	6.5
Zn	10	–	–	10[6]	16	20	37	330

[1] Förstner and Wittmann (1979) from refs. 2–7 and other studies; [2] Gibbs (1977); [3] Boyle et al. (1976); [4] Boyle (1978); [5] Trefry and Presly (1976); [6] U.S. Geol. Survey, Baton Rouge (1972/76); [7] Copeland and Ayers (1972); [8] Edgington and Robbins (1975); [9] Schroll et al. (1975), low water at six stations of the Austrian section; [10] Quentin and Winkler (1974): mean values 1971–1973; [11] Inst. f. Wasser-, Boden- und Lufthygiene. Bundesgesundheitsamt Berlin F.R.G. (unpubl. data, Working Group "Metals", German Research Society 1971/73).

luted, such as in the Lake Michigan area. An increase for most of the metals by a factor of approximately three, compared to the background values, is determined to be mainly the result of the influence of atmospheric contaminants (Klein, 1975). An indication of this is the characteristic increase in dissolved Pb-values in the water samples from Lake Michigan. Although the Danube River dewaters an area which is both densely populated and industrialized, very few of the trace elements are found to exceed the geochemical averages (Schroll et al., 1975); this seems also partly the consequence of the relatively high water discharge during most of the year. Similar metal concentrations have been observed in water from Lake Constance, which, being the largest drinking water reservoir in Europe, provides water for large regions of southern Germany. However, when compared to the background values of Table VI, first column, a four- (As, Zn, and Cu) to more than ten-fold (Hg, Ni, and Se) increase of the concentrations of trace elements can be determined.

The last column in Table VI refers to the lower Rhine River, which can be considered as one of the most heavily polluted large river systems on earth. Metals such as Pb, Fe, and Mn commonly exceed the acceptable maximum values for use as drinking water. In some cases Cd, Cr, Hg, and Se are present in critical concentrations. Between Lake Constance and the Dutch/German border, the concentrations of Zn and Cd increase by factors of 45 and 35, respectively (Heinrichs, 1975).

River–sea interface

A characteristic decrease of the dissolved-metal concentrations has been observed in the estuaries and has been partly ascribed to the "non-conservative" behavior of some of these elements (see Burton and Liss, 1976). This is due to the effects of coprecipitation with hydrous Fe-oxides and flocculation of organic substances (Sholkovitz et al., 1978). Such an effect is particularly pronounced in areas where rivers of low pH reach the sea. Studies performed by Foster et al. (1978) in the estuary of Afon Goch and Dulas Bay, North Wales, which drain an area mined for copper until the end of the last century, exhibit significant reduction of concentrations of dissolved transition elements at higher salinities. Examples of non-conservative removal of iron have been given by Coonley et al. (1971) from the Mullica River in New Jersey, estuaries in British Columbia (Williams and Chan, 1966), in three estuaries in southeastern U.S.A. (Windom et al., 1971), in the Gulf of St. Lawrence (Bewers et al., 1974), and in the Merrimack Estuary (Boyle et al., 1974). Fig. 4 gives examples from investigations of Duinker and Nolting (1977) showing the concentrations of dissolved species of Cu, Zn, and Cd at salinity values with the range of 0.4–35‰ in the estuarine mixing zone of the Rhine River. The decrease of the concentrations is explained by the removal from the dissolved state – relative to conservative mixing of freshwater and seawater – in the early stages of mixing: roughly 40% for Cd, 50% for Cu and 30% for Zn. No evidence of non-conservative behavior has been found for lead in the Rhine Estuary. However, the influence of the relatively clean seawater on polluted river waters during estuarine mixing should not be neglected. Müller and Förstner

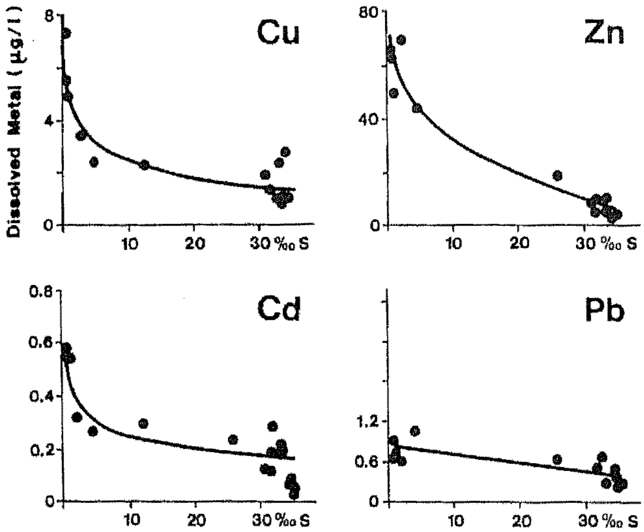


Fig. 4. Non-conservative behavior of Cu, Zn and Cd in estuarine mixing zones of the Rhine River in the Netherlands. (After Duinker and Nolting, 1977; with permission of Pergamon Press.)

(1975) found characteristic decreases of trace metal concentrations in the Elbe River approaching the North Sea (German Bight). Concentrations of Cd fell from 1.4 µg/l to 0.2 µg/l, Pb from 11.4 to 1.5 µg/l, Cu from 18 to 3.5 µg/l, Ni from 18.6 to 3.8 µg/l, Cr from 15.5 to 2.5 µg/l, and Zn from 194 to less than 10 µg/l. It seems that the decrease of dissolved (and solid) metal concentrations during estuarine mixing is strongest for those metals particularly enriched by civilizational effects, e.g., from domestic and industrial effluents.

METAL ENRICHMENT IN MINE EFFLUENTS

Mine effluents and tailings from mining and processing of ores represent a major source of heavy metals released to the environment and may have serious effects on the water quality of rivers and lakes, as well as on any biotopes, particularly on the fish populations (for further information on this subject, see Aplin and Argall, 1973 and Down and Stocks, 1977). One of the first descriptions of the problems arising from the strong enrichment of toxic trace elements both in dissolved and solid phases, is found in the Report of the 1868 River Pollution Commission in Britain, which studied the dispersal of metals from lead, zinc, and arsenic mines in mid-Wales (cit. Lewin et al., 1977):

> "All these streams are turbid, whitened by the waste of the lead mines in their course; and flood waters in the case of all of them bring down poisonous slime which, spreading over the adjoining flats, either befoul or destroy grass, and thus injure cattle and horses grazing on the dirtied herbage, or, by killing the plants whose roots have held the land together, render the shores more liable to abrasion and destruction on the next occasion of high water."

There are many examples of deleterious effects of mine effluents on freshwater ecosystems. In some streams of *Wales* enrichments of Pb, Cu, and Zn leached from the outcrops of mineralized zones and spoil heaps of disused mines still cause a high mortality rate in fish and other organisms (Abdullah and Royle, 1972). As early as 1924, Carpenter suspected that the complete lack of fish in several rivers in the Aberystwyth District of Cardiganshire could be the consequence of the pollution by the nearby lead mines. The unproductivity of certain fields in north Cardiganshire was explained by Griffith (1918) as a result of toxic levels of Pb and Zn in the soils. More recent investigations by Abdullah et al. (1972) on the distribution of transition metals in Welsh rivers clearly reflect the influence of mineralization zones. The rivers and lakes in regions where no mineral deposits are known, show Cd-levels ranging between 0.1 and 0.6 μg/l, whereas the annual average Cd-levels in rivers of the mineralized regions are found to range between 1.2 and 4.7 μg/l, with the highest recorded concentration being 20 μg/l. There seems to be a characteristic influence from this area on the waters of the adjacent Irish Sea (Fig. 5). The highest concentrations of Cd in the Bristol Channel are possibly derived from industrial effluents entering the area from the Avon and Severn Estuary. In Cardigan Bay, however, which is relatively free from industrial effluent and, because of a low population density, little domestic waste is present; runoff from the mineralized zones and sites of former mining activity is the main source of cadmium and of other trace metals (Abdullah et al., 1972). Laboratory tests and natural evidence indicate a distinct toxicity of waters from past and present mining areas of *southwest England* due to elevated concentrations of Cu, Pb, As, and Zn. Experiments on the Pacific oyster (*Crassostrea gigas*) with Zn-rich mine-adit water ranging between 100 and 500 μg/l reveal a decrease in growth, an increase in mortality rate (90% of the larvae died within two days at 500 μg/l Zn), and an increased incidence of abnormal larvae (Brereton et al., 1973). Oysters placed in the heavily contaminated Restronguet Creek contained initially 250 ppm Cu in dry matter, rising to 1500 ppm after one month, 2500 ppm after two months, and 6000 ppm after six months (Thornton, 1977). Data supplied by Anderson et al. (1976) from the Tamar Valley in the west of England suggest a significantly greater prevalence of dental caries in young residents of the Bere Alston area, where the soils are heavily contaminated by lead.

Studies related to the chemical composition of present mine drainage from the "Erzgebirge" in *Saxony* (East Germany), which has been exploited for centuries (ore processing dates back to the middle ages), have revealed that there is practically no plant growth in the vicinity of the major mine districts. The soils surrounding these areas have been markedly enriched with As and Pb, and mine drainage from percolation contains high levels of Pb, Zn, and in many cases, Ba (Leutwein and Weise, 1962). Flood-plain sediments of the Innerste River, originating in the Goslar–Oker area of the *Harz Mountains* in Germany, exhibit concentrations of Pb and Zn up to 20,000 ppm; poisoning of animals (e.g., cattle) by these deposits had been reported as early as the 18th and 19th centuries (Nowak and Preul, 1971). In *Poland*, Pasternak (1973, 1974) investigated the waste

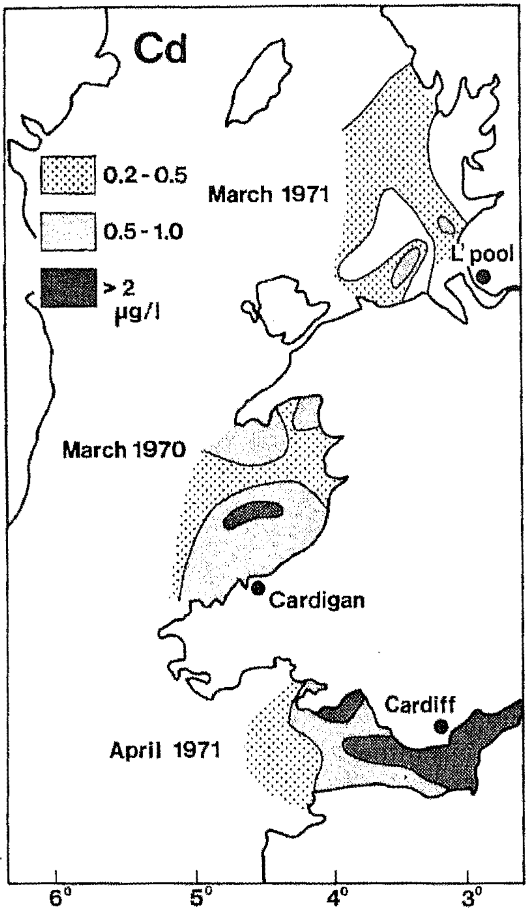


Fig. 5. Cd-enrichment in waters of the Irish Sea derived from industrial, domestic and mine waste effluents. (After Abdullah et al., 1972.)

waters from the regions of the Bolesław and Miasteczko Slaskie (Upper Silesia), where large deposits of Pb and Zn are mined and processed. The undergound water from the mine at Bolesław, which discharges directly into the Sztoła River, is enriched with Pb and Zn at maximum values of 300 mg Pb/l and 1800 mg Zn/l; the concentrations of Pb and Zn in flotation effluents reached 10.3 mg Pb/l and 1.7 mg Zn/l, respectively (Pasternak, 1973). The process of self-purification in some of the receiving waters is inhibited by the high concentrations of several metals as well as by the content of suspended material which prevents the penetration of light to the aquatic organisms. During the last few years no fish has appeared in the Sztoła River and the development of various algae is very poor (Pasternak, 1974).

Drainage water and stream sediments below the cinnabar mine at *Mount Avala near*

Belgrade (Serbia/Yugoslavia) have an abnormally high metal content, particularly of Fe, Ni, Hg, and As. The As-content in the Topciderska Reka stream was found to be up to 25 mg/l; the concentrations of Hg in the river sediments were as high as 6000 ppm. The very fine particles rich in As and Hg eventually reach the Danube and are deposited upstream of the Iron Gate Dam (Maksimović and Dangić, 1973).

In the *United States of America* the increasing awareness of the environment since the 60's has led to the recognition that metal accumulation in mine effluents is one of the main problems of water protection. In *Colorado* alone, 450 miles of surface streams are classified as affected by mill tailings and metal drainages (Wentz, 1974). Elevated contents of Ag, V, and other metals at Loma (Station of the Federal Water Pollution Control Administration; Kopp and Kroner, 1968), the station farthest upstream on the Colorado, stem partly from active mines and uranium plants at Rifle, Grand Junction and Gunnison. Part of these radioactive tailings have been utilized as landfill in construction projects and some 3000 homes in Grand Junction had to be abandoned since the highly penetrating γ-rays and Rn decay product could increase the risk of lung cancer to the inhabitants (Edsall, 1974; Anonymous, 1975). The high V-content in the Colorado River is probably due to the activities of an oil-shale extraction plant at Rifle. During the last few years particular attention has been devoted to the pollution effects of Mo in surface waters in the vicinity of the Mo-mining areas of Climax, Colorado (Runnels, 1973; Thurmann, 1974; Kaback, 1976). In Idaho, it is mainly the Kellog Smelterville area in Silver Valley (Miller et al., 1975) and the Cataldo Mission Flats in the catchment area of the Coeur d'Alene River (Galbraith et al., 1972) that are most affected by metal pollution. Airborne sources, consisting of particulates from smelter stack and dust blowing from smelter operations, as well as leachates from tailing ponds, contribute to an increase in the metal concentrations in the adjacent rivers, as has been repeatedly demonstrated in the Coeur d'Alene district (M. Ellis, 1940; Mink et al., 1972; Filby et al., 1974; Johnson et al., 1977; Rabe and Bauer, 1977).

Investigations in *Arizona* carried out by the U.S. Geological Survey (Durum et al., 1971) revealed extreme rates of increase for Cd (up to 130 μg/l), Co (4500 μg/l), and Zn (42,000 μg/l) in the Mineral Creek near Big Dome which could be attributed to the influence of acidic mine effluents (see below). Mining activities in the new lead belt of *Missouri*, the world's largest lead mining district, still pose some problems for water quality despite modern processing methods, as there is obviously a considerable metal transport by fine particulates (Jennett and Wixson, 1977). In the Mississippi drainage system, the *Tennessee River* gained particular attention due to the pollution influences from mining activities in the northern Tennessee zinc district (Derryberry, 1972; Perhac, 1972, 1974; Hildebrand et al., 1975). Acid mine drainage from abandoned pyrite mines in the North Anna River area of *Virginia* effected elevated concentrations of trace metals in water, sediments, and biota (Blood and Reed, 1975): the dissolved metal concentration in Contrary Creek were found to be up to 1580 μg/l for Cu, 190 μg/l for Pb, and 2670 μg/l for Zn. The concentrations in fish muscle tissue were as high as 22.7 mg Pb/kg and 16.9 mg Zn/

kg, which are among the highest reported values.

Comparable developments have also been reported from many mining areas of *Canada*, especially in those with sulfidic mineral occurrences, and particularly in places where, due to the lack of carbonates, the water has a low buffer capacity. Characteristic increases of heavy metals in freshwater systems result from atmospheric emissions containing both elevated contents of SO_2 and trace metals. An example is the Clearwater Lake in *Ontario* where the Ni-, Zn-, and Cu-concentrations are significantly higher than in the anthropogenically less-influenced Blue Chalk Lake (Dillon et al., 1977). From lakes near Sudbury, where very strong atmospheric inputs from smelter emissions occur, Wright and Gjessing (1976; data partly from Beamish, 1976) report dissolved concentrations of Ni and Cu of as much as 1850 μg/l and 1120 μg/l, respectively. Harvey (1976) has reviewed several examples of acid pollution problems from *Brunswick* mines: one of the worst cases where valuable fish resources were destroyed is the Brunswick No. 6 mine; the wastewater had the composition of 389 mg Zn/l, 31 mg Cu/l, and 131 Mg Fe/l, with a pH of 3.0 (Anonymous, 1972).

Deleterious metal inputs from mining activities include the discharge of tailings into *fjords*, such as those in *British Columbia*. D.V. Ellis (1977) described conditions in the Island copper mine near the north-end of Vancouver Island; Littlepage (1975) investigated the deposition of Mo-tailings in Alice Arm, on the northern mainland of the British Columbian Inlet; and Thompson (1977) cites the examples of two mining sites on Howe Sound and Rupert Island. In western *Greenland* deposits of mining waste contribute considerably to metal enrichments in fjord sediments (Bondam et al., 1976). In bottom waters of the Agfardlikavsa Fjord, Pb concentrations of up to 1000 μg/l have been recorded (Thomson, 1975). The pollution problems in the Sörfjord of western *Norway*, a 40 km long north–south extension of the Hardanger Fjord, were investigated by Skei et al. (1972, 1973). Three industrial factories, including a Zn-smelting plant, are reported to have released their metal-bearing wastes into a relatively shallow area of the fjord. During the period of investigation, approximately 100 tonnes (= metric-tons) of Cu, 1500 tonnes of Pb, and 2000 tonnes of Zn per year were discharged, strongly affecting the metal concentrations in the organisms (Stenner and Nickless, 1974). In green algae, the Pb concentration was 300 times greater, whereas Cd- and Zn-concentrations in mussels were 4–70 times greater than normal levels.

The most serious case of metal poisoning of humans by mine effluents is known from *Japan*. During 1947 an unusual and painful disease of a "rheumatic nature" was recorded in 44 patients from villages on the banks of the *Jintsu River*, Toyama Prefecture, Japan (Friberg et al., 1974). During subsequent years, it became known as the "itai-itai" disease (meaning "ouch-ouch") in accordance with the patient's shrieks resulting from painful skeletal deformations. It is estimated that approximately 100 deaths occurred as a result of the disease until the end of 1965. However, the cause of this disease was completely unknown until 1961 when sufficient evidence led to the postulation that Cd played a role in its development (Hagino and Yoshioka, 1961). It was found that the source of Cd-pollution of the Jintsu River was a zinc mine owned by the Makioko Co. situated some 50 km upstream from the afflicted villages. During World War II production of Zn and Pb from the mine was increased without sufficient accompanying treatment of the plant effluents and flotation sludge. The sludge from the plant became deposited downstream and caused considerable damage to the rice crops, which were irrigated or flooded by water from the Jintsu River. All patients were found to reside within 3 km of the river bank and in the low-lying rice-field areas which had been flooded by the polluted river water. After the mine constructed a retaining dam in 1955, pollution of the Jintsu River and the number of itai-itai cases rapidly declined. However, analytical data from the beginning of the 70's still indicated enhanced Cd-values in this area (Goto, 1973): 1 μg Cd/l in well water, 5–61 μg Cd/l (average 17 μg Cd/l) in mine waste water, and 1–9 μg Cd/l in river water.

The effects of the *Togane arsenic mine* north of Nagoya (Gifu-Prefecture) on the water of the Wada River was studied by Kato et al. (1973) from March 1972 to February 1973. The As-concentration in the river water was usually less than 30 μg/l. However, during the high-water period a maximum value of 1440 μg/l was determined near the closed mine (the mine ceased operations in 1957).

The earliest mining activity in the *Philippines* may be traced to ancient times when copper and gold had been traded and bartered between the Chinese mainland and other countries in Southeast Asia. At the turn of the century, after the American occupation, prospecting and mining activities were intensified, mainly in the mines of Mt. Province, Masbate, Surigao and in the Lepanto copper mines in Baguio (Lesaca, 1977). The latter region particularly suffers from the large quantities of mine tailings, which – despite provisions for settling ponds – still are partially disposed of into rivers, thereby causing excessive siltation (30,000 hectares of riceland have already been affected) and river quality degradation which affects agriculture and fishery resources.

Similar deleterious consequences on ecosystems have been reported from the disposal of mining wastes in Bougainville, *Papua New Guinea* (M.J.F. Brown, 1974). The influence of the Tui mine, Te Aroha and Maratoto silver mines in *New Zealand* on natural vegetation and inhabitants was investigated by Ward et al. (1976, 1977), who found some degree of pollution in the immediate vicinity of mining and processing plants.

A recent ecological survey conducted to evaluate the effects of a disused copper–lead–zinc mine at the Molonglo River in *Australia* (Weatherly and Dawson, 1973) revealed that the area is still disfigured by slime dumps, some 35 years after a flood that conveyed an enormous amount of tailing deposits from the mine area to the fairly productive adjacent flats. Today, 15 km downstream along the *Molonglo River*, the area is a virtual wasteland, whereby the release of zinc is regarded as the chief detrimental influence. Another example of large-scale destruction of organic life has recently occurred at *Rum Jungle* in northern Australia, 64 km south of Darwin, where U and Cu have been mined since the mid-1960's. An estimated 1300 tons of Cu have been released and dispersed onto the River Finiss floodplain. In addition, 90 curies of Ra, whose fate is still uncertain, has been leached from the tailing dump (Watson, 1975). A program to determine the immediate input of a new nickel refinery on metal levels in *Halifax Bay, North Queensland* is presently being performed by Knauer (1977). The refinery is located adjacent to the central part of the Great Barrier Reef and is continuously discharging liquid waste at the rate of some $15 \cdot 10^6$ l/day. The tailings contain significant quantities of Ni, Co, Fe, and Mn; Knauer (1977) found 130 μg/l Co and 1320 μg/l Ni in artifically prepared tailing supernatants.

Despite the relatively short history of Sn- and W-mining in *Tasmania,* the sparsely populated island has nevertheless suffered from mining activities. The coarse tailings and supernatants have caused Pb-, Zn-, Cu-, Mn-, Fe-, and H_2SO_4-enrichment in the *South Esk River* system, far beyond the borders of the mining areas (Tyler and Buckney, 1973). It was found that bordering farmers were unable to utilize the water from the creeks containing these mining effluents; fish and other biota were found to be even absent in some areas. Other parts of the river system less affected by the tailings still indicate a drop in both species diversity and abundance after winter floods, probably due to periodic movements of Cd and Zn down the river (Thorp and Lake, 1973). Analyses of the concentrations of Cd, Cr, Cu, Pb, Hg, Zn and other trace metals in filtered waters, suspended particulates, sediments, shellfish, airborne particulates, and sewage performed by Bloom and Ayling (1977) have shown that the *Derwent Estuary* of Tasmania is one of the most polluted areas of the world. Metallurgical liquid effluent discharges into the Derwent began several decades ago when an electrolytic Zn-refining plant went into operation. Dust falling in residential areas of Hobart contained up to 1450 ppm of Cd and 30,000 ppm of Pb. Approximately 42,000 ppm of Pb and 100,000 ppm of Zn were found in sediments near the wharf of the Zn-refining company. The highest ever recorded concentrations of Zn in oysters – 38,000 ppm dry weight – have been reported from the Derwent Estuary.

Finally, the investigations performed by Wittmann and Förstner (1976a, b; 1977a, b) indicate large-scale pollution by mine effluent from *Witwatersrand Goldfields in South Africa.* Here 247 slime dams are situated in a belt stretching approximately 120 km from Randfontein in the west to Nigel in the east (the total gold strike is over 380 km in length, containing seven goldfields). The levels of dissolved Mn, Co, and Ni exceed the normal surface water values by a factor of more than 10,000 for each individual metal; Fe, Cr, Zn, and sulfate concentrations are increased 1000-fold, whereas Pb and Cd in many instances are encountered at values exceeding a 100-fold enrichment. A comparison of these metal concentrations with drinking water standards reveals that the maximum values of all metals determined in gold/uranium mining effluents significantly surpass the permissible levels. The high Zn and Pb values are attributable to the cyanidation process for the recovery of Au, whereas high Mn values result from the oxidation of uraninite by pyrolusite (MnO_2) in sulphuric acid medium. However, tucholite, described as an "enigmatic hydrocarbon" (Feather and Koen, 1973) is a common cause of uraninite loss. It is therefore not surprising that the environmental impact from the uranium recov-

TABLE VII

Metal concentrations in inland waters affected by acidic mine effluents (examples)
All values in $\mu g/l$

	Cornwall (SW England)	Silesia (Poland)	Siberia (U.S.S.R.) [6]	Colorado (U.S.A.) [7]	Philippines [8]	Tasmania [9]	South Africa [10]
As	250 [1]	–	499	70	–	–	–
Cd	–	1,325 [4]	207	70	–	6,100	52
Co	–	13 [5]	368	–	–	–	3,300
Cr	–	17 [5]	–	–	120	–	4,000
Cu	1,160 [2]	62 [5]	20,710	3,900	953	1,350	5,400
Fe	23,000 [2]	3,185 [5]	–	213,000	176,100	20,500	550,000
Mn	2,400 [2]	315 [5]	1,624	8,000	–	22,500	206,000
Ni	–	14 [5]	900	460	80	–	6,400
Pb	530 [3]	23 [5]	2,071	300	443	–	290
Zn	10,000 [2]	43,100 [4]	5,770	17,000	1,280	105,000	26,000

[1] Tamar River (Aston et al., 1975); [2] Carnon R; [3] Gannel R. (Aston et al., 1974); [4] Granisczna Woda, inflow to [5] Mala Panew (Pasternak, 1974); [6] Maximum values from up to 4500 water samples (Udodov and Parilov, 1961); [7] Hill (1973); [8] Baguio Mining District, Agno and Bued Rivers (Lesaca, 1977); [9] Storys Creek in South Esk catchment (Tyler and Buckney, 1973); [10] West Driefontein Mine, West Wits Goldfield (Wittmann and Förstner, 1977a).

ery does not rest directly with heavy metal toxicity and pollution, but rather with the hazards associated with radioactivity (Wittmann, in Förstner and Wittmann, 1979).

A compilation of typical examples from the areas mentioned above is presented in Table VII. It is clear that these data of dissolved metal concentrations, which exceed by far the metal contents known from industrially or domestically influenced waters, are related to the occurrence of acid conditions in an aquatic system. The major process affecting the lower of pH-values (down to pH 2 to 3) is the exposure of pyrite (FeS_2) and of other sulfide minerals to atmospheric oxygen and moisture, whereby the sulfidic component is oxidized to sulfate (SO_4^{2-}) and the acidity (H^+-ions) is generated. Bacterial

TABLE VIII

Factors of environmental change from pollution by mines (After Jennett and Foil, 1979)

Mine waters
- Inorganic nutrients in the subterranean water
- High levels of CO_2 and carbonates
- Fuel spills
- Oil spills
- Hydraulic fluid spills
- Small mineral particles in mine effluent that produce turbidity
- Blasting agents – spills and partially oxidized compounds containing nutrients
- Highly variable mineral content of ore

Mill waters
- Chemical spills, both organic and inorganic
- Variable mineral content of ore may cause:
  - (a) Excessive use of reagents and loss of toxic chemicals to effluent
  - (b) Low recovery of heavy metals during pulses of very rich ore chemical reagents not adsorbed to concentrate and heavy metals are released in effluent
- Improperly placed concentrate piles allow dispersal of heavy metals either aerially or during runoff.
- High suspended and dissolved solids in effluent

Solid wastes
- Dams constructed of tailings wash directly into streams or blow onto soil and enter stream during runoff.
- Concentrated ore washes directly from storage piles into stream system or is blown onto soil and enters stream during runoff

Transport emission
- Concentrate-hauling vehicles are uncovered and high concentrations of heavy metals are blown onto soil and enter streams during runoff

Smelter emission
- Particulates build up into soil layer and enter stream during runoff

Tailings ponds
- Improper design relating to placement of ponds; insufficient size or number
- Insufficient retention time
- Release of toxic milling reagents to streams
- Release of organic and inorganic nutrients to streams
- Release of finely ground rock and mineral particles to streams

action (here *Thiobacillus ferroxidans*) can assist the oxidation of $Fe^{2+}(aq)$ in the presence of dissolved oxygen. Water seeping from mine refuse has been passing increased metal concentrations into water for decades. The threat is especially great in waters with little buffer capacity, i.e., in carbonate-poor areas where dissolved-metal pollution can be spread over great distances. A compilation of factors which might effect environmental changes by mining activities is given in Table VIII from a study by Jennett and Foil (1979). The authors have studied the impact of the world's newest and largest Pb–Zn mining district, the "New Lead Belt" or "Viburnum Trend" of southeast Missouri on an unpolluted stream basin, which was until recently virgin woodland. It is shown that run-off transport is a major factor in moving heavy metals from one ecosystem to another. In this case, Cd was almost completely solubilized, Pb was generally particulate-associated, and Zn was approximately one-half dissolved.

There are many different *pathways* for the release of heavy metals from tailings (Andrews, 1977): (1) structural failures from improper operational techniques and design in regard to possible stimulus of catastrophic events, such as earthquakes and floods; (2) direct discharges of mill waste effluent or total tailing to surface waters; (3) dust from unstabilized, desiccated, wind-blown surfaces; (4) biological concentration in plants and ultimately in animals; (5) erosion of embankment surfaces; (6) leaching to the surface via capillary action due to a high groundwater level or leaching to subsurface waters by permeation.

CONCLUSIONS

Of the data on the heavy-metal contents in fresh water, the aspect of geochemical exploration has not been considered to any great depth, although it was this field which influenced to a great extent the development of water analysis for heavy metals, mainly in the search for useable mineral deposits. For some years now prospecting has been done with the aid of solid substances in water bodies for measurements on fluviatile sediments and, more recently, on lacustrine sediments. These methods will be discussed in another chapter of this Handbook (see Chapter 4 in this volume).

If the data presented here is evaluated under the aspect of water pollution, the following conclusions can be drawn:

Of all the sources of toxic heavy-metal pollution in inland waters, the waste water from sulfide ore processing plants presents a particular problem: as a consequence of the oxidation of these minerals and the consequent low pH, the concentration of a number of heavy metals can rise inordinately. The result of these changes have been known for over 100 years, and yet it is still very difficult to effectively protect water systems against these pollutants.

Methods of controlling the problem of acidic mine drainage include thermodynamic measures (elimination of oxygen and the maintenance of reducing conditions, e.g., by application of sewage sludge on the surface of the spoil heaps), kinetic effects (e.g., changes of the bacterial propagation cycle leading from Fe^{2+} to Fe^{3+} – in an abiotic system, the oxidation of ferrous iron is roughly a factor of 10^{-6} slower than in a system mediated by bacteria), and especially, the application of bactericides (Singer and Stumm, 1970). The environmental consequences and controls of tailings were reviewed by Andrews (1977), whose study includes proposals for seepage collection and handling, underwater disposal and alternative tailings disposal in order to reduce or prevent the release of toxic metals into surface waters. In the future, the possibility of applying physicochemical methods to water processing, as is presently being applied in other fields of metallurgy (e.g. electroplating), will have to be further investigated. Apart from the widely used neutralization and electrolysis methods, three others have shown promising results: Hill et al. (1971) have developed a system in collaboration with the U.S. Environmental Protection Agency whereby the waste stream is neutralized, the sludge removed and the neutralized water returned to the influence of a *reverse osmosis unit*, a procedure referred to as *neutrolysis* (Hill, 1973). Metals can also be effectively removed from mine drainage by *cementation*, i.e. by the electromotive force of other metals, e.g., by passing the Cu-bearing water through shredded iron. Further, favorable results can be expected from ion-exchange methods, particularly in diluted solutions.

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