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The topic of this paper is extremely broad, and to allow more useful discussion, emphasis is placed on trace (less than 1 mg/l) metals in fresh surface waters and in drinking waters. An attempt is made to give a broad overview of current knowledge, problems and research with particular reference to the following: (1) metals of interest, current standards of water quality relevant to health, and concentrations of metals in waters; (2) sources of, and other factors affecting, the concentrations of metals; (3) general problems in the measurement of metal concentrations; (4) important research topics.

1. Introduction

Interest in trace elements in water has grown markedly over the last decade or so, mainly through increasing concern about the many undesirable effects known or suspected to be caused by certain elements. However, the possibilities of lack of biologically essential elements and protective effects of other elements must be borne in mind (Masironi 1976; Safe Drinking Water Committee 1977). Analysis of lake sediments, ice sheets, museum specimens, peat and other materials with chronological significance has indicated increasing concentrations of certain toxic elements, for example Hg and Pb (O.E.C.D. 1974; Waldron & Stöfen 1974; Jenkins 1976; Förstner 1977), over the last century, though some caution in interpreting such data appears to be necessary (Carr & Wilkniss 1973; Sikes & Drain 1973). It has also been suggested (Stumm & Bilinski 1973; Imboden & Stumm 1973) that man's global activities now lead to greater inputs of Ag, Au, Cd, Cr, Cu, Hg, Pb, Sb, Sn, Tl, and Zn than the amounts safely disposed of naturally, mainly by deposition in the oceans. (See also Förstner & Müller (1974) and Goldberg (1975, 1976) on this topic.)

The topic 'trace metals in waters' is vast, and would require a treatise of many volumes to deal reasonably thoroughly with all relevant aspects. The present paper is therefore intended merely to summarize certain points considered by the author particularly relevant to environmental geochemistry and health. The treatment is necessarily superficial, but the aim has been to quote references that will allow deeper consideration of each point. Attention has also been confined to trace metals in fresh and drinking waters, the term 'trace metals' signifying here those metals and metalloids usually not exceeding concentrations of 1 mg/l; radionuclides are excluded (I.A.E.A. 1975). A number of other, more detailed, reviews of similar scope but concerned primarily with fresh surface waters has appeared recently (Hem 1970; Andelman 1973; Leckie & James 1974; Williams *et al.* 1974; Förstner & Müller 1974; Wilson 1976).

Of course, the emphasis here on fresh waters does not mean that estuarine and sea waters are not important. Recent and comprehensive discussions of trace elements in such waters may be found, for example, in Hood (1971), Riley & Skirrow (1975), Riley & Chester (1976), Burton & Liss (1976) and Goldberg (1976).

2. Water quality standards for trace metals

Many problems are involved in establishing appropriate, realistic and numerically defined standards for the concentrations of trace metals in drinking waters. For example, the chronic effects of ingestion of water containing very small concentrations of contaminants are difficult to establish, particularly when one must consider all members of the population with their differing susceptibilities owing to age, drinking habits, and other characteristics. The situation is complicated by the possibility of synergistic and antagonistic effects between different metals. Further, the effect of an element may depend on its chemical form as with the different toxicities of inorganic and organic forms of Hg, the different oxidation states of As, etc. Finally, there are difficult questions such as the extent to which metals in water used to prepare food and drinks are ingested, the relation of the intake from water to that from food, air and other sources, and the relative availabilities to man of metals in water and other sources. Research into such topics is in hand by many teams throughout the world, and advances are being made. However, it seems to the author that it will be many years before water quality standards can be regarded as being on a completely sound basis in all respects. Nevertheless, in considering water resources and their treatment and distribution as drinking water, some guidance on the quality that may, on the best evidence available, be considered suitable seems to the author essential. Current water quality standards provide that guidance, and are therefore a useful means of providing an overview of the metals (and their concentrations) of current interest.

Many countries have their own standards for water quality, and these have not always been established by the same procedures and do not always agree with each other in all respects. For example, the U.S.S.R. standards for drinking water (Stöfen 1973) include a number of metals on toxicological grounds while a recent study in the U.S.A. (Safe Drinking Water Committee 1977) concluded that numerical standards for certain of those metals were either not necessary or could not be defined with the information available at present. In this situation, rather than attempting to give a catalogue of the standards of many different countries, the recommendations of the World Health Organization on the trace metals content of drinking water (W.H.O. 1970, 1971) are shown in table 1. These drinking water standards are the basis of, or are similar to, those of many countries. The traditional approach of the United Kingdom has been not to have numerically defined standards for drinking water (Martin 1972), but entry to the European Economic Community has changed the picture. A Community Directive on the quality of surface water intended for drinking water is now in force (Council of the E.E.C. 1975), and a proposal for a Directive on the quality of drinking water is under discussion (Commission of the E.E.C. 1975). The trace metals in these two Directives are also shown in table 1.

Table 1 shows that a number of elements are of interest from the viewpoint of health. Recent reviews may be consulted for details of the effects – real, suspected, or worthy of investigation – of the individual metals; see, for example, Masironi (1976) and the Safe Drinking Water Committee (1977). It is also worth noting that, of the five elements listed in table 1 as 'undesirable', Masironi (1974) has suggested that Cu, Zn and Mn are worthy of study in investigations of the relation between water quality and cardiovascular disease. For that and other reasons (Masironi 1974, 1976), Li and Sr are also of interest. Finally, Al and Mn in water have been suggested as possible causal factors of dialysis encephalopathy (Platts *et al.* 1977). Lest table 1 be interpreted as proof of the harmful effects of metals generally present in drinking waters, three points should be emphasized here. First, the problems of formulating standards mentioned above should be borne in mind. Secondly, at the concentrations normally present, a number of the metals may have beneficial effects. Finally, though positive correlations between the concentrations of certain metals and the incidence of diseases have been observed, this by no means necessarily implies that the metals are the causal agents.

Table 1. Water quality standards (micrograms per litre)† for undesirable or toxic trace metals

	drinking water			surface water
element	W.H.O. European 1970	W.H.O. International 1971	E.E.C. proposed 1975	E.E.C. 1975
toxic				
antimony	—	—	10	—
arsenic	50	50	50	50
barium	1000	?	100	100
beryllium	?	?	?	?
cadmium	10	10	5	5
chromium	50‡	—	50	50
cobalt	—	?	?	?
lead	100	100	50	50
mercury	?	1	1	1
molybdenum	?	?	—	—
nickel	—	—	50	?
selenium	10	10	10	10
silver	?	—	10	—
tin	?	?	—	—
uranium	?	?	—	—
vanadium	?	?	?	?
undesirable§				
aluminium	—	—	200	—
copper	50	50	100	50‖
iron	100	100	200	300‖
manganese	50	50	50	50‖
zinc	5000	5000	100	3000‖

? Metal mentioned in standards as needing control, but insufficient information available to specify a numerical value.

† Various provisos have been omitted for simplicity; see the original publications. The quoted values represent the maximum acceptable concentration (or similar concept).

‡ Chromium (VI).

§ Usually not of toxicological significance at concentrations normally present.

‖ Greater values allowed depending on the treatment applied to the water.

Standards for the quality of surface waters are also required for purposes other than the production of drinking water. For certain elements, these other purposes may require more stringent standards. For example, the U.S.S.R. standard for Mo in drinking water is 500 μg/l (Stöfen 1973), whereas a value of 5 μg/l has been recommended in the U.S.A. for water to be used for continual irrigation (F.W.P.C.A. 1968). Similarly, the protection of fisheries may require much smaller values than those in table 1 for Zn in river waters. In this connection, the possibility of indirect effects of water quality on health through progressive accumulation of toxic metals in food chains should also be noted.

Mention should also be made that Hg, Pb and Cd have been identified as the three priority elements to be measured in the U.N.E.P./W.H.O./U.N.E.S.C.O./W.M.O. Global Water Monitoring Project (Inter-Agency Working Group on Monitoring 1974).

Thus, many metals are of interest at concentrations whose measurement is beset with several important problems. These difficulties have an important bearing on the amount and accuracy of published information on metal concentrations in water. Before considering these problems, it is useful first to consider briefly both the nature and the sources of metals in waters.

3. Species of metals present in waters

The above standards do not generally state explicitly the metal species of interest, but the normal approach is to consider the total concentration of all species of a given metal. However, to understand the distribution, behaviour and effective properties of metals in waters, consideration of the chemical and physical forms present is essential (Stumm & Bilinski 1973; Andelman 1973; Wilson 1976; Cantillo & Segar 1975; Florence & Batley 1977; Stumm & Morgan 1970). Stumm & Bilinski (1973) have given a useful classification of the types of species that occur in waters, and table 2 is based on their scheme.

Table 2. Types of metal species in water†

metal species	examples	metal species	examples
(1) free metal ions	$Cu(H_2O)_6^{2+}$	(6) colloids	FeOOH
(2) simple radicals	UO_2^{2+}, VO_3^-	(7) metals sorbed on colloids	Pb on clays
(3) inorganic complexes	$CdCl^+$, $CuCO_3^0$ $Pb(CO_3)_2^{2-}$	(8) precipitates, mineral particles	$PbCO_3$, PbS
(4) organic complexes, chelates and compounds	$Cu\text{-}OOC.CH_3^+$ $Hg(CH_3)_2$	(9) metals in live and dead biota	metals in algae
(5) metals bound to organic materials of high molec. mass	Pb-fulvic acid polymers		

† Based on Stumm & Bilinski (1973); the size of the metal species increases in passing from type 1 to type 9. Types 1–4 are in true solution and type 5 is transitional.

In addition to the species shown in table 2, many metals can exist in different oxidation states that commonly show markedly different speciation. Thus, the oxidation state may govern whether a metal is present as an anionic or cationic species, for example Mo, V and Cr. The solubility and tendency to complexation of a metal may also depend markedly on its oxidation state, for example Mn and Fe. Interconversion of the various species may occur, and the nature and extent of such conversions depends on the pH, the inorganic and organic constituents of a particular water, and the biota present. Such effects can have many important consequences (Wilson 1976). For example, the discharge of an effluent into a river may, if the pH is changed or if the effluent contains metal-complexing substances, affect equilibria between metals in sediments and in the overlying water. The mobility and effects of metals in rivers may be markedly affected by such processes (Dietz *et al.* 1975; Förstner & Patchineelam 1976; McDuffie *et al.* 1976; Farrah & Pickering 1977; Singer 1977; Gardiner 1975). Natural processes may also lead to changes in the species present. Thus, algal blooms in lakes and reservoirs can lead to relatively large metal concentrations in the biotic phase; thermal stratification of water bodies may also cause deoxygenation of bottom waters and consequent appearance of dissolved forms of iron and manganese in their lower oxidation states (Hutchinson 1975).

Methods for measuring the concentrations of the different forms of a metal in waters, and the results from such studies are considered in §§6*b* and 7*a* respectively.

4. Sources of trace metals in fresh waters

(*a*) *Surface waters*

The main sources of trace metals are summarized below, but it should be remembered that the effects of these sources on the concentrations of metals in a water are also governed by the speciation of the metal in the water.

(i) *Atmospheric precipitation*

Dust, rain and snow may represent very important, direct sources of metals to water bodies (Winchester & Duce 1977). For example, Hem & Durum (1973) have suggested that lead in rainfall may be one of the dominant factors affecting the concentration of Pb in the rivers of the U.S.A. As might be expected, industrial smelting plant may contribute metals such as Zn and Cd to nearby water bodies (Van Loon & Beamish 1977), but airborne contaminants may also be transported long distances before precipitation. Numerous publications give data on trace metal fallout (see, for example, Cawse 1974; Oliver *et al.* 1974; Müller & Beilke 1975).

In addition to the direct input of metals, other atmospheric contaminants (for example, sulphur oxides) may affect metals in waters by decreasing the pH and thereby leaching metals from sediments (Beamish & Van Loon 1977).

(ii) *Geochemical sources*

Weathering of surface soils and rocks is a potential source of many trace metals to waters. The natures and concentrations of these metals have been reported by some authors to depend on local geological and geochemical factors (Aston & Thornton 1975, 1977; Förstner & Müller 1976; Förstner 1977). Other authors (for references, see Wilson 1976) have concluded that dissolved metal concentrations are not generally well correlated with geological factors. Such apparent discrepancies probably arise because of the many factors affecting metal concentrations and their distribution between water and sediments.

Ore bodies and past and present mining activities may cause unusually high concentrations of particular metals in surface waters (Jorden & Meglen 1973; Thornton & Webb 1975; Förstner & Wittmann 1976). Spring waters of deep-seated origin may contribute elements not usually found in surface waters, for example Ge (Silvey 1967).

(iii) *Effluents*

Generalization on the effects of industrial effluents is impossible because they clearly depend on the nature of the industry and its effluent control procedures. Such effluents can be important sources of metals such as Hg (O.E.C.D. 1974). Effluents from sewage treatment plants also contain trace metals; of the many papers, those by Helz *et al.* (1975), Adams *et al.* (1975), Roberts *et al.* (1977) and Perry *et al.* (1975) give useful information.

One aspect that has recently received growing attention is the quality of water draining from urban areas during heavy rainfall. Such water may contain very high concentrations of metals, and particularly those such as Pb that settle on urban surfaces from the air (Wilber & Hunter 1977; Water Research Centre 1977*c*). Effluent discharges may also release metals from sediments (see §3 and (iv) below).

(iv) *Sediments*

Sediments commonly contain much greater concentrations (by mass) of metals than the overlying waters. The metals in sediments are generally present as small mineral particles or are absorbed on, or coprecipitated with, other undissolved materials. Such undissolved forms of metals usually contribute rather little to metal concentrations in the water, but changes in water quality, natural or man-made, may lead to the release of metals from sediments (see §3). One interesting example is the release of Hg as a dissolved chloride complex when high concentrations of chloride from road de-icing enter waters (Feick *et al.* 1972).

(v) *Land drainage*

The general geochemical effect of the soil is noted in (ii) above, but man's activities may also be important; for example, the use of chemicals in agriculture, deposition of contaminants from the atmosphere, use of sewage sludge as a fertilizer (Sommers 1977; Jennett & Linnemann 1977; Huang *et al.* 1977), and leaching of waste tips (James 1977) may all cause contamination of surface waters.

(*b*) *Groundwaters*

In general, less attention appears to have been paid to the trace metals present in groundwaters (Edmunds & Morgan-Jones 1976). Of course, such waters contain trace metals through natural processes, but pollution may also occur through processes such as those mentioned in (*a*) above. Some authors (for example, Silvey 1967) have argued that the concentrations of trace metals will tend to be greater in groundwaters than in surface waters because of the greater biological activity of the latter. In addition, groundwaters may contain trace metals derived from deep strata and ore bodies not contacted by surface waters (Silvey 1967; Shvartsev *et al.* 1975). However, as for surface waters, the crucial factors controlling metal concentrations seem more likely to be generally the chemical equilibria governing the speciation and solubility of a metal (Hall 1974; Shvartsev *et al.* 1975; Edmunds 1977). Natural or man-made sources of metals at or near the land surface may be rendered less important through removal of metals as water percolates through the ground. The pollution of groundwaters and its control have been the subject of recent conferences (Water Research Centre 1977*a*; Bureau de recherches géologiques et minières 1977).

(*c*) *Control and variability of metal concentrations*

Consideration of the many sources of metals mentioned above suggests two important conclusions.

First, when assessing means of controlling metal concentrations, the total environment should be considered (Suffet 1977). Complete elimination of one source may be of little or no value if the major sources remain uncontrolled. It is encouraging, therefore, to note the increasing attention being paid to the control of atmospheric pollution, toxic chemicals, waste tips, effluent disposal, etc.

Secondly, sources of trace metals show marked temporal variability, both systematic (for example, seasonal) and random. Thus, it would be expected, and measurement confirms, that metal concentrations in waters will tend to be very variable with time; relative standard deviations of reported concentrations are commonly 100% or more. The nature of this variability may also depend on the metal species present. For example, in rivers, dissolved forms may decrease in concentration with increasing flow rate (dilution effect) while the converse may be true for undissolved forms (sediment entrainment). The effect of flow-rate on the total concentration of a metal may therefore be quite different from the effects on the dissolved and undissolved fractions depending on their relative concentrations (Hellmann 1970). In addition to temporal variability, the spatial distribution of sources of metals means that metal concentrations may differ markedly from one water body to another, and from one point to another within the same river or lake. The consequences of such variabilities are considered in §6*a*.

5. SOURCES OF TRACE METALS IN DRINKING WATERS

For systems where a treatment plant supplies an area with drinking water through a piped distribution system, there are three main sources of trace metals in the water received by the population.

(*a*) *Raw waters*

The sources of trace metals in raw waters have been mentioned in §4. The steadily growing demand for water is increasingly restricting the choice of suitable sources of water, and greater use must be made of waters actually or potentially liable to contamination (Dick & Packham 1976). Although control of sources of pollution within catchment areas of water sources is receiving increasing attention, special interest also attaches to the extent to which trace metals are removed by water treatment plant.

At present, most treatment plants have not been chosen with regard to removal of metals, and the processes involved vary from plant to plant depending on other characteristics of the water. The removal achieved by a given process depends on the metal and its speciation (Brezonik 1974; Singer 1974) and on the process conditions. For example, the removal of certain metals in coagulation processes can depend markedly on whether or not the metals are organically bound (Shapiro 1964), and on the pH at which precipitation processes are operated (Stumm & Bilinski 1973; Brezonik 1974). The efficiency of a given process may therefore vary from one type of raw water to another. Table 3 gives some broad indications of the efficiency of certain treatment processes. See also Hannah *et al.* (1977) for a recent paper on this topic.

(*b*) *Treatment plant and chemicals*

The materials of construction of the plant and the chemicals used for treatment are potential sources of trace metals. Few detailed investigations appear to have been made of such sources, and further studies are desirable. As one example, the chemicals used in the U.K. have been estimated to contribute no more than 1 μg/l of Pb (Ainsworth *et al.* 1977). Of course, treatment by coagulation may well lead to increased concentrations of Fe or Al.

TABLE 3. REMOVAL OF METALS IN TREATMENT PROCESSES†

metal	removal efficiency (%)‡ alum coagulation	lime softening (pH 9.5–10)	activated carbon
arsenic (As III)	0–30	0–30	0–30
arsenic (As V)	60–> 90	60–90	0–30
barium	0–30	60–90	0–30
cadmium	0–60	> 90	> 90
chromium	0–30	—	> 90
cobalt	0–30	60–90	60–90
copper	60–90	—	—
lead	60–90	> 90	60–90
mercury (CH_3HgCl)	0–30	0–30	> 90
mercury ($HgCl_2$)	0–30	30–60	60–90
molybdenum	0–30	—	—
nickel	0–30	60–90	30–60
selenium (Se IV)	0–30	0–30	0–30
selenium (Se VI)	0–30	0–30	0–30
silver	—	—	> 90
strontium	0–30	—	—
tin	—	—	> 90
vanadium	—	—	30–90
zinc	0–30	60–90	0–60

† Data from Alexander *et al.* (1954), Logsdon *et al.* (1974) and the Safe Drinking Water Committee (1977); efficiencies for other processes are also given in these references.

‡ The removal efficiencies should be regarded as only semi-quantitative indications, and can depend markedly on the particular operating conditions of a process.

(*c*) *Materials of the distribution system and domestic plumbing*

A variety of materials is used for the pipes and other components of the distribution system; concrete, iron, steel, asbestos-cement, and polyvinyl chloride are most commonly used. Such materials may contribute major components such as Fe and Ca to the water, but much less is known of the extent of leaching of minor components. Further investigation of this aspect is required, and is proceeding in many laboratories. Leaching of Pb from unplasticized PVC pipes is one example where appreciable concentrations of a minor component may enter the water, but fortunately this effect is short-lived (Ainsworth *et al.* 1977).

Similar points apply to the materials used in domestic plumbing systems. However, these materials include a number that may be important sources of metals such as Pb, Cu, Cd and Zn (Craun & McCabe 1975). Of special concern is the widespread occurrence of lead piping and other components (Department of the Environment 1977). However, depending on the quality of the water and whether or not it is chemically treated to reduce its plumbosolvency, protective carbonate and other coatings may be formed (Ainsworth *et al.* 1977). Thus, the presence of lead components does not necessarily imply the presence of substantial concentrations of Pb in water; a similar point applies to other materials. Again, many laboratories are studying the many aspects involved in controlling the pick-up of metals from domestic plumbing systems (see, for example, Department of the Environment 1977).

(*d*) *Control and variability of trace metals in drinking waters*

Possible means of control have been indicated in (*a*)–(*c*) above.

Towns and cities often have a number of raw waters and associated treatment plant, and the materials used for the distribution and domestic plumbing systems often vary in different areas of a town, and in individual houses. These and other factors can lead to marked spatial variability of metal concentrations throughout a distribution system. The sources of the metals are also affected by many factors that vary with time (Packham & Wilson 1977). Thus, marked variability of metal concentrations is commonly observed.

6. MEASUREMENT OF TRACE METAL CONCENTRATIONS

The need for reliable data on metal concentrations requires no emphasis, but the processes of sampling and analysis face many problems. Failure properly to recognize and overcome such difficulties and/or fully to quote details of procedures and accuracy of results means that, in the author's view, much published information is of very poor and/or unknown accuracy. This position is now steadily improving, and though discussion is not appropriate here, this paper would be incomplete without brief mention of the main problems.

(a) *Accuracy of analytical results*

Relevant aspects have been reviewed by Wilson (1974), and more recent papers are quoted below.

Given the large temporal variability of metal concentrations, estimates of their central tendency and variability are subject to large uncertainty when based on only a few samples. Spatial variability leads to a similar problem. The times and locations of sampling, therefore, need careful consideration. Lettenmaier & Burges (1977) and Hines *et al.* (1977) discuss this problem for surface waters; for groundwaters and drinking waters, see Water Research Centre (1977*a*) and Packham & Wilson (1977), respectively. The interpretation of results must also take into account the frequency distributions relevant to metal concentrations (Wilson 1976; Mage & Ott 1976).

Results may be completely invalidated by contamination of samples during and after collection, and metal concentrations in samples may also show a marked tendency to decrease through, for example, absorption on the walls of sample containers. Such problems can be overcome by appropriate procedures (Batley & Gardner 1977; Moody & Lindstrom 1977).

Innumerable inter-laboratory tests have repeatedly shown that analytical accuracy is much worse than expected; errors of 200–300 % are quite commonly found (McFarren *et al.* 1970). To control accuracy, special analytical quality control tests should be used as an integral part of the work of any laboratory. An approach used in the U.K. in monitoring river water quality has been described by Simpson (1978) and Wilson (1978, 1979), and has also been applied to drinking water (Ranson & Wilson 1976).

(b) *Determination of metal species present in waters*

The importance of this topic is emphasized throughout this paper, and comprehensive reviews of the relevant procedures are available (Wilson 1976; Florence & Batley 1977). Great difficulties face attempts to measure the concentrations of the different forms of a metal. Although some useful guides may be obtained from theoretical calculations based on stability constants (Morel *et al.* 1973), ignorance of the interactions of metal ions with many of the constituents of waters (for example, colloidal materials) restricts the value of this approach. Practical approaches employ various separation and measurement techniques, but the results obtained are perhaps best regarded at present as relating to 'operationally defined' fractions rather than to particular species. Further research is needed to assess the general value of such results but present indications are that they provide useful information in considering the behaviour and effects of trace metals. Most of this work has so far been applied to natural waters but research on drinking waters is now beginning.

Filtration through membrane and other filters is often used to separate 'dissolved' and 'undissolved' forms of metals. Considerable caution in interpreting such results is necessary; undissolved forms may pass through filters, and dissolved forms may be removed by them.

7. Trace metal concentrations in waters

Given the many factors affecting the species and concentrations of metals in waters, it is difficult to give a reasonably accurate yet simple summary of published information. The following sections are intended, therefore, to give only broad indications, and are no substitute for experimental measurements when particular waters are of interest.

(*a*) *Forms of metals present*

Almost all published work appears to have dealt with surface waters, but the results seem likely to apply to some extent to drinking waters.

(i) *'Dissolved' and 'undissolved' forms*

From a review of published information on river waters, Wilson (1976) suggested the following broad generalizations:

mainly 'undissolved': Co, Fe, Hg;
mainly 'dissolved': Ba, Li, Sr;
variable behaviour: Cd, Cr, Cu, Pb, Mn, Ni, Zn.

(ii) *More detailed schemes of fractionation*

The few detailed studies have been concerned mainly with Cd, Cu, Pb and Zn. They have shown clearly that the 'dissolved' forms of these metals are distributed among several different fractions, and that the distribution is markedly dependent on the metal and the composition of the water. The results suggest certain generalizations; for example, Cd tends to exist in labile, inorganic forms whereas Cu does not and tends rather to be associated with organic materials (Stiff 1971; Gardiner 1974; Florence 1977). However, much more research is required on both techniques and applications before attempting any firm conclusions (Guy & Chakrabarti 1975).

(*b*) *Concentrations of metals present*

(i) *River waters*

From a critical review of the literature, Wilson (1976) estimated the broad ranges within which metal concentrations commonly fall; a single figure to represent the approximate central tendency of the concentrations was also given. These estimates are given in table 4 but it is stressed that they were derived by subjective judgement rather than explicit statistical procedures. However, similar estimates have been given by other authors, and details of these as well as information on many other elements may be obtained from the reference.

Table 4. Metal concentrations in river waters

metal†		approximate concentration/(μg/l) range‡	central value‡	metal†		approximate concentration/(μg/l) range‡	central value‡
arsenic	(?)		0.4	manganese	(D)	1–100	5
barium	(T)	2–200	40	mercury	(T)	< 1	< 0.5
beryllium	(D)	< 0.3	< 0.3	molybdenum	(D)	0.2–20	5
cadmium	(D)	0.1–10	1	nickel	(D)	0.5–50	10
chromium	(D)	0.2–20	3	silver	(?)	0.01–1	0.1
cobalt	(D)	0.1–10	0.5	strontium	(T)	10–1000	250
copper	(D)	0.5–50	7	tin	(?)		0.04
iron	(D)	3–300	40	uranium	(T)	0.1–10	1
lead	(D)	1–100	5	vanadium	(D)	0.1–10	3
lithium	(T)	1–100	10	zinc	(D)	2–200	20

† Estimates of Wilson (1976, p. 36) except for arsenic, silver and tin, whose values were taken from the references there cited. The letters T and D denote total and 'dissolved' concentrations, respectively; ? denotes that the forms of metals measured were not stated.

‡ The limits of the range are not minima and maxima; see text for significance of the values quoted.

(ii) *Groundwater*

Much less information appears to have been published on trace metals in groundwater, but inspection of a number of papers indicates that the ranges of concentrations given in table 4 are reasonable for most elements. For Fe and Mn, greater concentrations – quite commonly greater than 1 mg/l – occur in aquifers subject to reducing conditions. Shvartsev *et al.* (1975) give a useful tabulation of the concentrations of 36 trace elements.

(iii) *Drinking waters*

In the past, few trace metals have been measured routinely in the drinking water from consumers' taps; with the exception of Pb, rather little information exists, and much of this is difficult to interpret (see, for example, point 2 below). This situation is changing, and we can look forward to much more information in a few years. For example, the Water Research Centre, under contract to the Department of the Environment, has started a survey of many trace metals in the drinking water of a number of towns (see also Craun & McCabe 1975). At present, however, it seems wise not to attempt any firm conclusions on the concentrations of metals in drinking waters, and in place of this some broad impressions are given below.

(1) Metals present as major constituents of materials used in the distribution and plumbing systems tend to show greater concentrations at consumers' taps than in the treated water before distribution (Craun & McCabe 1975; Department of the Environment 1977). Pb, Cu, Zn and Fe often show this behaviour, but other metals may also show the effect. The magnitude of this 'pick-up' depends on many factors (Packham & Wilson 1977), but in some towns it results in a substantial proportion of households whose drinking water may exceed the standards in table 1. The known, toxic effects of Pb make this element of special concern at present (Department of the Environment 1977).

(2) For elements such as those in point 1 above, it is difficult to characterize the quality of drinking water (Packham & Wilson 1977). Care is also essential in interpreting published information. For example, Zoetman & Brinkmann (1976) quote the average concentrations of Pb for a number of European cities, but such averages may grossly overestimate the

concentrations for households with lead-free plumbing; equally the concentrations for houses with lead may be underestimated.

(3) Apart from elements such as those in point 1 above, the others of interest appear usually to fall within the ranges given in table 4. For those elements for which numerical standards exist (see table 1), there appears to be no common tendency for the standards to be exceeded, though isolated instances may occur (McCabe *et al.* 1970; Hammerstrom *et al.* 1972; Craun & McCabe 1975).

(4) The concentrations of trace metals in drinking water can differ markedly from one town to another. More study is needed to establish all relevant factors, but geochemical factors appear to be directly responsible for certain elements. For example, raw waters in calcareous areas tend to contain greater concentrations of Sr which is incompletely removed by any treatment plant (Alexander *et al.* 1954). Lithium seems likely to be another such element. In addition to direct geochemical effects, other water quality characteristics (for example, pH and carbonate alkalinity) may affect the magnitude of pick-up of trace metals in plumbing systems. The often-quoted plumbosolvency of soft waters is thus an example of an indirect geochemical effect.

8. Conclusion

The preceding sections have stressed the many factors affecting the concentrations and forms of trace metals in drinking waters, the present lack of knowledge on many of these factors, and the difficulties in measuring trace metals. In addition, the effects on health of many of the trace metals at the concentrations present in drinking waters are largely unknown (Groth & King 1976; Safe Drinking Water Committee 1977). Research into many of these topics is at an early stage, and it is premature to attempt a firm assessment of the importance of environmental geochemistry in relation to the health effects of trace metals in drinking waters. Nevertheless, a few concluding remarks on two aspects of this question may be useful.

First, it is clear that geological factors may directly affect the concentrations of certain metals in drinking water, but the general importance of such factors for many metals is not known. Of course, these factors do contribute trace metals to fresh waters, but there are many other sources; in addition, the mobility of metals in natural waters, their removal in water-treatment plant, and their pick-up in distribution and plumbing systems may well govern the concentrations finally appearing at consumers' taps. What is required now is detailed study of the concentrations of trace metals in many drinking waters and location of the sources of the metals found. Such work is now proceeding in a number of laboratories including the Water Research Centre; it will be greatly helped by the application of sophisticated analytical techniques capable of the simultaneous measurement of the many trace metals of interest (Water Research Centre 1977*b*).

The second and even more difficult aspect concerns the effects on health of trace metals in drinking waters. There is general agreement that the concentrations of certain toxic elements with no known beneficial function (for example Cd, Pb and Hg) need to be controlled at levels which may sometimes be exceeded in drinking waters, but even for these elements there is considerable uncertainty on the health effects of their ingestion from drinking water. For many other metals, there is no firm knowledge that the concentrations present in drinking waters cause any effects at all. Commins (1978) has made a preliminary study of the contribution made by drinking water to the total human intake of a number of elements in the U.K. He concludes that only four metals (Ba, Pb, Li and Sr) may contribute as much as 10–20 %, though he notes that the biological availability of elements in water may be greater than in food. Masironi (1976) has stressed that the observed correlations between certain metals and incidence of disease indicate only the need for further study and do not imply that the metals are causal agents. Many authors have stated that much more research – epidemiological and other – is necessary (Groth & King 1976), and it is encouraging to see such work expanding in many countries. The value of a multi-disciplinary approach to these studies has been emphasized by Groth & King (1976). One example of such an approach is the collaboration of teams from the Royal Free Hospital and the Water Research Centre in a new and detailed investigation of factors affecting the incidence of cardiovascular disease (Shaper 1976; Dick & Packham 1976).

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