

Occurrence of metals in waters: An overview

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Abstract

Presence of metals in natural, drinking and waste waters can imply two types of circumstances (depending on concentration and specific metal): firstly, certain positive effects, especially, when the metals present in drinking water are essential for human life (e.g. Mo and Zn); secondly, some negative and toxicologically undesirable effects for both human consumption and the general environment (i.e. Cd, Hg).

This paper gives an overview of outstanding aspects related to the chemical behaviour, occurrence, physiology and toxicology of the 25 metals most frequently found in waters: Aluminium, antimony, arsenic, barium, beryllium, boron, cadmium, calcium, chromium, cobalt, copper, iron, lead, lithium, magnesium, manganese, mercury, molybdenum, nickel, potassium, sodium, selenium, silver, tin and zinc.

On the other hand, the maximum concentrations of metals in natural, drinking waters and waste waters are listed according to the actual Spanish regulations. Finally, references to the maximum levels of metals in drinking waters established by a recent proposal of Directive in the European Union, as well as the latest WHO's guideline values for metals have been also considered.

Introduction

The concentrations of metals in water are a function of the particular chemical and electrochemical behaviour, as well as other conditions of the hydrological environment. These levels can vary from a few ng/l (10^{-9} g/l) or $\mu\text{g/l}$ (10^{-6} g/l) in those known as **trace metals** (i. e. beryllium, cadmium, mercury...) to mg/l (10^{-3} g/l) or even in some cases g/l , with respect to the **major metals** (calcium, magnesium, sodium).

On the other hand, the effects of the different metals present in waters range from beneficial (calcium, zinc) through troublesome, to being dangerously toxic in certain cases (lead, mercury). Thus, some metals are essential, while others may adversely affect water consumers, waste-water treatment equipment and systems, and receiving waters.

Summarising, some metals may be either beneficial or toxic, depending on their concentrations and physiological behaviour.

Along the following, we provide an overview of the occurrence, toxicology and other aspects of the 25 different metals most frequently found in the water environment.

Aluminium

Atomic number 13
Symbol Al
Atomic mass 26.982
Oxidation number for dissolved substances:
+1(aluminous ion), +3(aluminic or aluminate ions).

Al is one of the more common elements in the earth's crust, at 8.1% by mass. Al in waters emanates from the dissolution processes of natural silicates; it can be found either as soluble salts or as colloidal compounds (Driscoll, 1985) ranging in concentration between 0.10 and 10 mg/l .

The behaviour of Al in natural waters is a function of the erosion phenomenon of siliceous rocks which yield, firstly, colloidal Al, and later, dissolved Al (especially, Al^{3+}). Furthermore, this metal can form a variety of complexes such as AlF_6^{2-} and AlCl_4^- (Hemm, 1986) and complexes with acetic, citric, tartaric and oxalic acids. Sparingly soluble salts of this metal are phosphate, oxinate and calcium aluminate (Pourbaix, 1966).

Al levels in river water can vary widely and a range of 0.012 to 2.250 mg/l has been reported for USA rivers (Driscoll, 1985; Neal, 1994). In areas where acidic deposition has occurred, surface water with depressed pH values exhibits Al levels in the range of 0.10 to 0.80 mg/l (Driscoll, 1985).

With respect to lakes and reservoirs, the Al levels increase slightly with depth during the thermal stratification period, with higher ranges during the mixing period (**turnover**) (Fig.1 (a)). Thus, the total concentration of metal in water is related to the input of rich clays to lake water (Driscoll, 1985; Marín Galvín, 1991 a-c). Conversely, very important increases of total Al in deep waters of reservoirs which experience strong anoxic conditions in depth during the stratification period (Fig.1 (b)) can be detected (Marín Galvín, 1995).

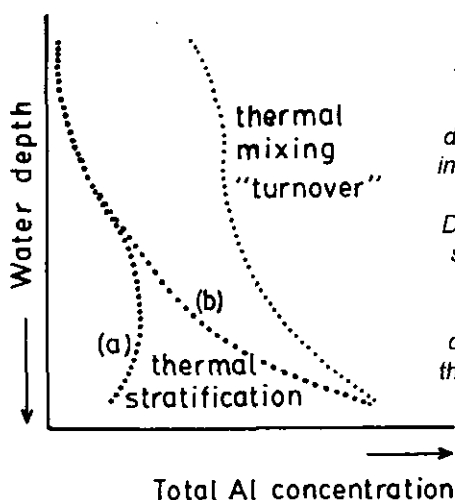


Figure 1
General depth dynamics for total Al in a typical temperate zone reservoir. Dynamics during the stratification period can evolve in two different forms, depending whether the anoxic conditions in depth are moderate (a) or marked (b)

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TABLE 1
MAXIMUM CONCENTRATIONS OF METALS IN WATERS (AS mg/l) ACCORDING TO SPANISH REGULATIONS

Metal	(a)	(b)	(c)	(d)	(e)	(f)
Al	0.200	-	2.00	1.00	-	-
Sb	0.010	-	-	-	-	-
As	0.050	0.10	1.00	1.00	-	(1)
Ba	0.100	1.00	20.00	-	-	-
Be	-	-	-	0.50	-	-
B	1.000	1.00	10.00	2.00	-	-
Cd	0.005	0.005	0.50	0.005	-	(1)
Ca	100.00	-	-	-	-	-
Cr	0.050	0.05	4.00(3)	5.00	-	(1)
Co	-	-	-	0.20	-	-
Cu	3.000	1.00	10.00	0.20	0.04(2)	(1)
Fe	0.200	2.00	10.00	2.00	-	-
Pb	0.050	0.050	0.50	5.00	-	(1)
Li	-	-	-	5.00	-	-
Mg	50.00	-	-	-	-	-
Mn	0.050	1.00	10.00	2.00	-	-
Hg	0.001	0.001	0.100	-	-	(1)
Mo	-	-	-	0.005	-	-
Ni	0.050	-	10.00	0.50	-	(1)
K	12.00	-	-	-	-	-
Se	0.010	0.010	0.10	0.05	-	-
Ag	0.010	-	-	-	-	(1)
Na	150.00	-	-	(4)	-	-
Sn	-	-	10.00	-	-	-
Zn	5.000	5.00	20.00	-	0.30(2)	(1)

- (a) drinking water
- (b) raw water for drinking-water production
- (c) waste waters to public rivers
- (d) water for irrigation
- (e) fish life
- (f) mollusc growth.

- (1) lower concentration to that causing toxic effects in mollusc growth
- (2) for water with 100 mg/l CaCO₃ hardness
- (3) concentration expressed as tripositive chromium
- (4) Na concentration lower than 60% of the sum of these concentrations of (Na+K+Ca+Mg).

The presence of Al in natural and treated waters depends on its chemical properties (Pourbaix, 1966; Hemm, 1986). Due to the fact that aluminium hydroxide solubility shows a minimum at pH=5.07, in more acidic waters the aluminic ion (Al³⁺) is found, while the aluminate ion (AlO₂⁻) is formed at pH values higher than 9.00 (Pourbaix, 1966; Neal, 1994).

Al is a non-essential element from a physiological point of view (Trapp, 1986). The metabolism of aluminium in humans is not well understood, but it appears that inorganic Al is poorly absorbed, being rapidly excreted in the urine. The Al present in drinking waters is fundamentally the residual emanating from the use of Al compounds in flocculation processes. In this sense, the main problem of the metal with respect to ingestion by humans is based on the possibility of favouring the incidence of certain neurological disorders such as Alzheimer's disease, in renal dialysis patients treated with water obtained from drinking-water supplies rich in Al (WHO, 1981) (more than 0.11 mg/l). Nevertheless, the above is actually under revision (Suet-mei and Wing-shiu, 1992).

Table 1 shows the maximum Al levels and maxima for all those metals considered in this paper, in untreated, drinking waters and waste waters, according to Spanish regulations. Moreover, Table 2 presents the maximum concentrations of metals in drinking waters recommended in a proposal for a council directive of the European Union (EU, 1995) and by the WHO (WHO, 1993).

Antimony

Atomic number 51
Symbol Sb
Atomic mass 121.75

Oxidation number for dissolved substances:
+3(antimonyl and antimonite ions, meta-antimonous acid), +4, +5(antimonic ion).

TABLE 2 MAXIMUM CONCENTRATIONS OF METALS IN DRINKING WATERS ACCORDING TO: (a) PROPOSAL FOR A COUNCIL DIRECTIVE IN THE EUROPEAN UNION (1995) (b) PROVISIONAL GUIDELINE VALUES PROPOSED BY WHO (1993)		
Metal	(a)	(b)
Al	0.200	0.200
Sb	0.003	0.005
As	0.010	0.010
Ba	-	0.700
B	0.300	0.300
Cd	0.005	0.003
Cr	0.050	0.050
Cu	2.000	2.000
Fe	0.200	-
Pb	0.010	0.010
Mn	0.050	-
Hg	0.001	0.001
Mo	-	0.070
Ni	0.020	0.020
Se	0.010	0.010

This is a typical **trace metal** found in very small quantities in waters ($\mu\text{g}/\text{l}$). Two forms of Sb are found in natural waters: Sb^{3+} which occurs under moderately oxidising conditions and Sb^{5+} predominating in highly oxidising environments.

The source of Sb in the water medium is the dissolution of sulphide minerals which contain the element. In this way, Sb is also associated with arsenic minerals as impurity. Likewise, Sb can occur in some raw waters due to discharges from dye factories, mining effluents and certain other industries (*Standard Methods*, 1989; EUREAU, 1994).

According to the data available (WHO, 1993; EUREAU, 1994) Sb in drinking waters is usually less than $4 \mu\text{g}/\text{l}$ (as ions or organic complexes), while in certain parts of England and Wales the concentrations can be as high as $12 \mu\text{g}/\text{l}$. Where antimony-tin solder replaces lead solder, exposure to Sb may increase.

Sb is a non-essential element showing toxic character, but only at relatively high concentrations. In this sense and based on inhalation exposure, it can be concluded that antimony trioxide is possibly carcinogenic to humans and antimony trisulphide is not classifiable as carcinogenic to humans (WHO, 1993).

Arsenic

Atomic number 33

Symbol As

Atomic mass 74.91

Oxidation number for dissolved substances:

+3(arsenyl, meta- and mono-ortho- arsenite ions, and meta- and ortho- arsenious acids), +5(mono-ortho-, di-ortho- and tri-ortho- arsenate ions, arsenylic ion and ortho-arsenic acid), +7 (perarsenyl ion).

Arsenic is common in a great variety of minerals, as well as sulphides, specially in those of Cu, Co, Pb and Zn. The mean concentration of As in the earth's crust is about $2 \text{ mg}/\text{kg}$. The presence of As in waters is due to both soluble salts and organic complexes emanating from volcanic emissions. In this way, tartrates, molybdates and tungstates form complexes with arsenic. The alkali metal arsenites and arsenates are very soluble; the other arsenites and arsenates are soluble only in acid solutions. In particular, triargentic arsenate and magnesium ammonium arsenate are sparingly soluble in water (Pourbaix, 1966). Moreover, under moderately oxidising conditions arsenic is found as As^{3+} , while a higher oxidising medium promotes the oxidation toward As^{5+} .

Nevertheless, the main contribution of arsenic to waters is actually industrial, because of production of As as a by-product in the metallurgical processing of other metals.

The amounts of the metal present in waters are lower than some $\mu\text{g}/\text{l}$, in contrast, concentrations of mg/l can be tested in polluted underground waters (WHO, 1981). Recent data for Europe indicate that most groundwater sources have As values lower than $10 \mu\text{g}/\text{l}$, increasing up to $70 \mu\text{g}/\text{l}$ in some aquifers. In this way, the use of pesticides rich in As can be a source of metal to the water and general environment. While the majority of European surface waters present As values of less than $5 \mu\text{g}/\text{l}$, rarely exceeding $10 \mu\text{g}/\text{l}$ (EUREAU, 1994), higher As levels in groundwaters have been reported from many parts of the world, e.g. 0.6 to $2.0 \text{ mg}/\text{l}$ in Taiwan, $3.0 \text{ mg}/\text{l}$ in Japan, 0.9 to $3.4 \text{ mg}/\text{l}$ in Argentina and up to $1.7 \text{ mg}/\text{l}$ in the USA (Dutta and Chaudhuri, 1991).

Arsenic is bioaccumulated in aquatic organisms and it does not have a known physiological effect. The biological methylation of inorganic As compounds in the environment is sufficiently known. As has not been shown to be carcinogenic in bioassays in animal species, but it has been shown to induce chromosome aberrations in a variety of cultured cell types, including human cells.

Inorganic arsenic is a documented human carcinogen. In this form it penetrates organisms and undergoes a biotransformation to methyl-arsenic similar to the above-mentioned; thus, it can be accumulated in the renal system and skin. Ingestion of the metal causes irritation of gastric mucous membranes, muscular cramps and cardiological alterations sometimes resulting in death. On the other hand, accumulation of As in skin can cause pathological processes, and can contribute to skin cancer development (WHO, 1986-1993; Underwood, 1977).

Barium

Atomic number 56

Symbol Ba

Atomic mass 137.33

Oxidation number for dissolved substances:

+2(barium ion).

The amount of Ba in the earth's crust is about $0.5 \text{ g}/\text{kg}$, especially found in certain minerals such as **barite** (barium sulphate) and **witherite** (barium carbonate). Moreover, the Ba compounds are used in several industrial activities: petroleum wells, paints and paper pulp, bituminous products, medicine and others (WHO, 1986).

Salts of Ba sparingly soluble are the carbonates, oxalates, sulphates, phosphates and chromates while certain complexes such as polymetaphosphates and organic hydroxyl compounds are more soluble (Pourbaix, 1966).

Ba is found relatively frequently in waters at levels of less than 0.1 mg/l. Likewise, certain volcanic thermal waters can contain up to 10 mg/l (USEPA, 1977). On the other hand, the Ba concentration in drinking water does not exceed 1.0 mg/l and is commonly about 0.10 to 0.40 mg/l for USA and Russian drinking waters (WHO, 1986).

This metal is not essential for the human being. It is associated in the body with the calcium and magnesium of bones and in the renal system, liver and heart. From a physiological point of view, the effects of Ba ingestion depend on the type of salt: the acetate is non-toxic up to doses of 5 mg/l, while the chloride is toxic in even lower doses.

Excessive ingestion of Ba gives a stimulating effect to muscle tissue (WHO, 1986); indeed, several studies have proven a possible link between the consumption of waters with more than 10 mg/l of Ba and certain negative cardiologic effects (Brenniman et al., 1979; WHO, 1990a).

Beryllium

Atomic number 4
Symbol Be
Atomic mass 9.013
Oxidation number for dissolved substances:
 +2(beryllium, beryllate and diberyllate ions).

This metal is commonly associated with feldspars although it can also be found in a typical mineral such as "beryl" (USEPA, 1980). On the other hand, Be is uncommon in natural waters but it is sometimes found as the chloride, nitrate and sulphate salts. These compounds are relatively soluble in water in the following sequence: $Cl > NO_3 > SO_4$. Beryllium also forms soluble complexes with anions such as citrate, tartrate, oxalate, fluoride and phosphates.

In continental waters, the mean Be concentrations range from 10^{-2} to 1.1 µg/l, while in drinking waters it can be detected only at very low levels, commonly less than 1 µg/l and showing a mean level near to 0.2 µg/l (WHO, 1993). Moreover, this element can be found in the radioactive form as 7Be , emanating from natural interactions between cosmic radiation and the atmosphere (UN, 1988).

Beryllium can be concentrated by phytoplankton and those consuming it; thus, the levels in these can be increased more than 1 000 fold with respect to the original level in waters.

This metal appears to be poorly absorbed by the gastrointestinal tract and can probably be carcinogenic to humans through interactions with DNA, causing gene mutations and chromosome aberrations in cultured mammalian somatic cells, but not in bacterial test systems (WHO 1990b; 1993).

Boron

Atomic number 5
symbol B
atomic mass 10.82
oxidation number for dissolved substances:
 +2(hypoborate ion and hypoboric acid), +3(ortho-, meta- and tetra-borates and hexaborates ions and ortho-, meta-, and tetra-borics acids), +4,5(diborate ion),
 +5(perborate ion).

The main natural minerals containing B are **granites, pegmatites and borates**, specially sodium and calcium borate. On the other hand, the use of B for surfactant production actually represents a very important source of pollution by the metal, especially in industrial and municipal waste waters. Likewise, the use of pesticides, varnishes and paints rich in B can provide another way of discharging the metalloid to the environment (García Garrido, 1986). Boron forms numerous complexes with molybdates, tungstates, vanadates phosphates and arsenates as well as with all the organic hydroxyl compounds. Borates of metals other than the alkali metals are all sparingly soluble in water (Pourbaix, 1966).

Natural unpolluted waters show low B levels ranging between 0.01 and 0.05 mg/l. Conversely, waste waters and underground polluted waters can show higher B concentrations: more than 2.5 mg/l have been tested in some Spanish zones (Granada, Barcelona) (Marín Galvín, 1995). Recent data on the occurrence of B in European groundwaters indicated concentrations ranging between 0.02 and 0.82 mg/l, while in surface waters the levels measured increased up to 1.24 mg/l in some cases (England and Wales) (EUREAU, 1994) but showing mean values around 0.10 to 0.20 mg/l.

Ingestion of borate and boric acid is rapid and it is completely absorbed by the gastrointestinal tract and excreted through the kidneys. Although B has not been shown to be mutagenic in *in vitro* systems, it has a negative effect on the digestive and nervous systems in the human being (García Garrido, 1986); furthermore, the regular consumption of drinking water rich in B can cause death. Effluents of waste waters rich in the metalloid can be unfavourable to fish life, even causing death.

Finally, while B is an essential element for the correct growth of vegetables, irrigation water should not contain more than 0.75 mg/l of B (Catalán Lafuente, 1981).

Cadmium

Atomic number 48
Symbol Cd
Atomic mass 112.41
Oxidation number for dissolved substances:
 +2(cadmous, cadmite, bicadmite ions).

This is a **trace element** in the earth's crust which is generally associated with zinc minerals (i.e. **greenockite**, a cadmium sulphide found associated with zinc sulphide). The use of this metal for battery manufacture is actually decreasing due to the extreme toxicity of the metal.

Cadmium forms several complexes with anions: halides, nitrate, sulphate, ticsulphate, ammonia and cyanide, generally not very stable. A large number of salts and basic salts of Cd are sparingly soluble or very sparingly soluble, i.e., carbonate, cyanide, phosphate and sulphide (Pourbaix, 1966).

Form and fate of Cd in water depend upon its chemical speciation which is determined by the pH of the water and the hardness as well as the presence of ligands and co-existing metal cations. So, the solubility of Cd in water is a function of the pH value: the lower the pH value the higher the solubility. In this way, surface waters commonly show <1 µg/l (Catalán Lafuente, 1981; Hlat and Juff, 1973). Furthermore, the waters rich in humic compounds contain the lowest Cd levels because of the high stability of the Cd-humic substances complexes generated there (Standard Methods, 1989).

Cadmium is a metal which experiences a bioaccumulation process similar to that experienced by Hg. The metal is taken up by vegetables (usually rice and wheat) from polluted waters and subsequently ingested by humans and animals through food and water intake.

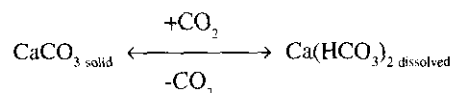
Liver and renal systems are the end organs of Cd in the body, and due to the very low excretion rate of the metal, Cd increases its level slowly in organisms. Toxicological effects of Cd depend on the amount ingested, ranging from stomach aches to severe lung damage. Moreover, prolonged exposure to Cd can cause renal and bone alterations. These disruptions cause "Itai-Itai", a disease detected in the Japanese town of Itai-Itai, as a result of the ingestion of Cd-polluted fish by humans. The fish had been exposed to Cd in the industrial waste waters of a zinc mine near the town (Hiat and Juff, 1975; ECC, 1979; WHO, 1986; WHO, 1992). Nevertheless, the carcinogenic effect of Cd salts by oral route has not been proven and the genotoxicity of the metal is not clear.

Calcium

Atomic number	20
Symbol	Ca
Atomic mass	40.08
Oxidation number for dissolved substances:	
	+2(calcium ion).

Calcium generally shows sparingly soluble salts such as bicarbonate, sulphate, chloride, fluoride, phosphate and chromate and is the main cation in waters. It can also form complexes with polymetaphosphates (i.e. EDTA), sugars, and citric acids. Calcium arises in water systems either by sulphate and silicate dissolution or due to the action of dissolved CO₂ in water on the Ca present in **limestones, dolomites and loams**.

In this sense, a typical phenomenon in waters is named the carbonic equilibrium: this comprises the reaction between the CO₂ dissolved in water and the very slightly soluble calcium carbonate to yield the more soluble calcium bicarbonate (Catalán Lafuente, 1981; Degrémont, 1979; Stumm and Morgan, 1980; Morel and Hering, 1993). There is a complex equilibrium between the amounts of CaCO₃, Ca(HCO₃)₂ and CO₂, characteristic for each water. When the water shows a certain pH value, the pH of equilibrium, the above species have a constant concentration. Thus, the water is inert in respect of the dissolution of CaCO₃ precipitate (which is saturated) to produce dissolved Ca(HCO₃)₂, or in contrast, the water does not precipitate CaCO₃ from the more soluble bicarbonate (García Garrido, 1986; Marín Galvín, 1995). The general chemical processes can be written as follows:



Calcium and also Mg form (approximately) the hardness of water. This parameter is very important to determine the use of water for drinking water, for industries, or for agricultural irrigation.

Levels of Ca in waters can be wide-ranging, but generally, they are in the range 10 to 20 mg/l. Likewise, underground waters contain more Ca than surface waters. Other sources of Ca to waters are those from numerous industrial effluents.

Calcium provides a certain taste in drinking water which depends on the specific salt present (Zoeteman, 1980; *Standard*

Methods, 1989). Moreover, the presence of Ca in water used on heat exchangers can produce undesirable effects due to corrosion or incrustation (Mullen and Ritter, 1974; Morel and Hering, 1993; Marín Galvín, 1995).

Finally, Ca has a relevant physiological action on bone formation and also on nerve integrity and transmission. However, the consumption of drinking water rich in Ca can provoke heart arrhythmicity. On the other hand, the habitual ingestion of waters poor in Ca is also not recommended (ECC, 1979).

Chromium

Atomic number	24
Symbol	Cr
Atomic mass	52.01;
Oxidation number for dissolved substances:	
	+2(chromous ion), +3(chromic, chromyl and chromite ions), +6(chromate, acid chromate and dichromate ions, and chromic acid).

Chromium is found in the mineral **chromite**. The Cr²⁺ ions form amine and cyanide complexes; the Cr³⁺ ions form complexes not only with chlorides, but also with fluorides, sulphates, ammonium salts, cyanides, sulphocyanides, oxalates and citrates; chromates are complexed by H₂O₂; the chromates of the alkali metals, and also ferric, cupric, manganous and magnesium chromates are soluble, but the majority of the chromates of the other metals are insoluble (Pourbaix, 1966).

From a chemical point of view, the Cr⁶⁺ salts (HCrO₄⁻; CrO₄²⁻ and Cr₂O₇²⁻) are more soluble than the Cr³⁺ compounds, especially the hydroxide. Oxidation of trivalent Cr to hexavalent Cr can be carried out electrochemically and, also, biologically. This implies a complex equilibrium between dissolution and precipitation of Cr compounds in natural water media. In this sense, the reductive action of organic matter on the Cr⁶⁺ compounds to yield Cr³⁺-organics complexes is well known (ECC, 1979; WHO, 1993).

The main sources of Cr to the environment are industrial effluents emanating from the production of corrosion inhibitors and pigments.

The concentrations of Cr in natural unpolluted waters are not higher than 25 µg/l (ECC, 1979); nevertheless, these levels increase for waters with low pH values (pH 6,0) as well as for very hard waters. On the other hand, total Cr concentrations in drinking waters are usually lower than 2 µg/l, although up to 0.12 mg/l have been reported in some cases (WHO, 1993).

Chromium is an essential **trace metal** involved in glucose metabolism as an insulin co-factor. Moreover, Cr has a beneficial action, increasing the protein and amino acid uptake by cells. Furthermore, excessive ingestion of Cr³⁺ is needed to cause toxicological disruptions in human beings, while lower ingestions of Cr⁶⁺ may promote skin alterations as well as pulmonary problems and even cancer (ECC, 1979; WHO, 1986). Finally, the mutagenic activity of Cr⁶⁺ compounds can be decreased by reducing agents, such as human gastric juice (WHO, 1993).

Cobalt

Atomic number	27
Symbol	Co
Atomic mass	58.93
Oxidation number for dissolved substances:	
	+2(cobaltous and dicobaltite ions), +3(cobaltic ion).

Typically a minor **trace metal** in both the lithosphere and the hydrosphere, cobalt forms soluble complexes with ammonia, chlorides, cyanides and sulphocyanides. Likewise, it forms insoluble salts with sulphides, carbonates, oxalates and cyanides (Pourbaix, 1966).

In natural waters concentrations lower than $1\mu\text{g}/\text{l}$ are commonly tested, ranging from 0.1 to $0.5\mu\text{g}/\text{l}$ (Catalán Lafuente, 1981; Morel and Hering, 1993). The main incidence of Co in waters is that of radiological concern as the isotopic form of ^{60}Co is a typical β -emitter (UN, 1988) in nuclear power stations.

Although cobalt shows toxicity in aquatic environment, it is not toxic to humans except at very high ingestion levels (i.e. in beer) and could cause in these cases cardiac disruptions. On the other hand, Co is a metal essential for humans and is needed for the formation of vitamin B_{12} which is necessary to synthesise haemoglobin in the body.

Copper

Atomic number 29
symbol Cu
atomic mass 63.57

oxidation number for dissolved substances:
+1(cuprous ion), +2(cupric, cuprite and bicuprite ions), +3(copper and cuprate ions).

Copper in nature is found either in the element form or in several compounds (oxides, complex sulphates, and carbonates). Monovalent Cu forms complexes with chloride, nitrate, ammonia and thiosulphate, and salts which are sparingly soluble such as cyanide, chloride, bromide, iodide and sulphocyanide. Divalent Cu forms complexes with chloride, amine, sulphocyanide, bromide, iodide, nitrate, oxalate and pyrophosphate, and soluble salts with the exception of ferrocyanide, sulphide and carbonate (Pourbaix, 1966).

On the other hand, concentrations of Cu lower than $1\text{ mg}/\text{l}$ (between 10 and $100\mu\text{g}/\text{l}$) are commonly found in raw waters, especially in association with organic colloids. Likewise, in waters rich in ammonia (NH_3 or NH_4^+) Cu can be found in a wide variety of **Cu-ammonium** complexes.

Waters poor in organic compounds e.g. in Germany, showed Cu concentrations ranging from 5 to $10\mu\text{g}/\text{l}$. Waters with highest amounts of organics such as Sweden, showed up to $390\mu\text{g}/\text{l}$ (EUREAU, 1994). However, drinking waters currently do not contain more than $0.50\text{ mg}/\text{l}$ of Cu.

Copper is an essential **trace element** for human being; it is involved jointly with Co and Fe in the production of haemoglobin and erythrocytes and, thus, in bone and nervous system formation. Furthermore, Cu is contained in some enzymes as the cytochrome and the ascorbic acid oxidase (ECC, 1979).

Several Cu compounds, as the sulphate, are very effective in water treatment to eliminate algae and other micro-organisms (*Escherichia coli*). This action is due to the obstruction by Cu of the cell walls of micro-organisms which are then incapable of taking up oxygen by themselves. Moreover, moderate levels of Cu in natural waters have a negative effect on some fish (like trout).

Copper is widely used in drinking-water network systems due to its chemical inertness. Nevertheless, highly oxygenated waters, which are relatively acidic or warm can contribute to the corrosion of Cu pipelines and increase the Cu levels in drinking waters (Mullen and Ritter, 1974). Concentrations of 3 to $5\text{ mg}/\text{l}$ of Cu provide a bitter or astringent taste and even an acute gastric

irritation in some individuals, as well as colour and turbidity effects if the level exceeds of $1\text{ mg}/\text{l}$ (ECC, 1979; Zoeteman, 1980; Catalán Lafuente, 1981; WHO, 1986).

Iron

Atomic number 26
Symbol Fe
Atomic mass 55.85

Oxidation number for dissolved substances:

+2(ferrous, hypoferrite and dihypoferrite ions), +3(ferric and ferrite ions), +4(ferryl and perferrite ions), +5(perferryl ion), -6(ferrate ion).

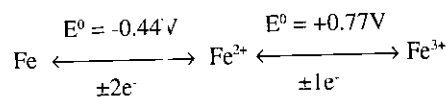
Iron is the fourth element in order of abundance on the earth. The main Fe compounds are divalent and trivalent salts such as hydroxides, carbonates and sulphides (Stumm and Morgan, 1980; Marín Galvín, 1981; Cirundl and Delwiche, 1993).

Divalent Fe forms the following complexes: amine complexes, with organic hydroxy compounds, hypophosphites, oxalate and with cyanide. Also, Fe^{2+} forms salts which are sparingly soluble such as carbonates, cyanides, oxalates, phosphates and sulphides. On the other hand, trivalent Fe is complexed by hydrochloric, sulphuric, thiocyanic and acetic ions generating complexes which are not very stable. In contrast, the complexes between Fe^{3+} and hydrofluoric, pyrophosphoric, phosphoric, organic hydroxyl and oxalic ions are more stable, the complexes with ferricyanide and ferrinitrosocyanide being very stable. Finally, phosphates and sulphides of trivalent Fe are sparingly soluble (Pourbaix, 1966).

Iron in water originates from both rock dissolution and minerals and steel production and other industrial waste waters. Iron in surface waters is generally in the Fe^{3+} form ranging between 0.1 to $0.3\text{ mg}/\text{l}$: this is due to the precipitation of $\text{Fe}(\text{OH})_3$ at $\text{pH} = 7.5$ and lower. The Fe^{2+} salts are more soluble and precipitation starts at $\text{pH} = 6.0$. Thus, underground waters rich in CO_2 and poorly oxygenated very frequently have higher concentrations of Fe (total) than surface waters. Likewise, if waters are rich in organic matter there are very stable **Fe^{2+} -organic matter** generated complexes which cause serious problems in the subsequent treatment of these waters (Degrémont, 1979; Tchobonaglou and Schroeder, 1985; Marín Galvín and Rodríguez Mellado, 1993). However, Fe is found in natural fresh waters at levels ranging from 0.5 to $50\text{ mg}/\text{l}$ (WHO, 1993).

In lakes and reservoirs, the dynamics of Fe evolves from low concentrations of total Fe in the entire water column during the thermal mixing period (waters well oxygenated) to higher levels of Fe (especially Fe^{2+}) in deep poorly oxygenated waters (thermal stratification) produced through biological or electrochemical reduction of Fe^{3+} precipitates present in muds and sediments of lakes (see Fig. 2). This behaviour is similar to that exhibited by phosphorus (WHO, 1986; Marín Galvín, 1995).

From a physiological viewpoint, Fe plays a very outstanding role: it is known for its presence in proteins (i.e. haemoglobin), cytochromes and several redox enzymes. In this case, Fe acts in the following global redox processes:



Ingestion of high amounts of Fe causes important reversible disruptions in several human tissues. The presence of the metal

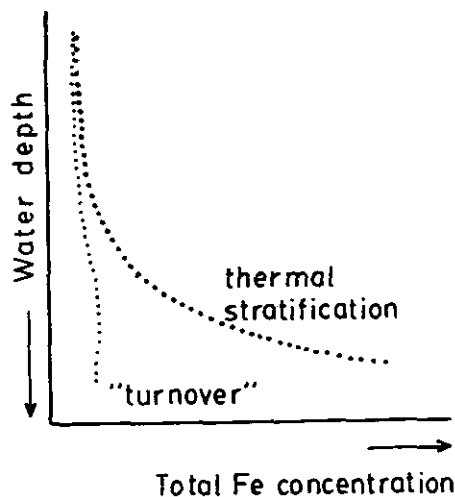


Figure 2
General depth dynamics for total Fe in a typical temperate zone reservoir

in drinking water, also as a result of the use of iron coagulants, leads to corrosion in network systems and consequently, off-tastes, colour and turbidity. In this phenomena certain ferric bacteria are also involved (Degrémont, 1979; Wetzel, 1981; Marín Galvín, 1995).

Lead

Atomic number 82

Symbol Pb

Atomic mass 207.0

Oxidation number for dissolved substances:

+2(plumbous, plumbite and biplumbite ions),

+4(plumbic, acid metaplumbate, meta- and ortho-plumbate ions).

The main Pb minerals are the sulphides and carbonates. This metal is widely used by man as an additive in fuels, production of batteries, paints, antiradiation armour, pesticide formulation and others.

The Pb^{2+} forms complexes which are slightly stable with nitrate, chloride and cyanide, and other fairly stable complexes with acetic, organic hydroxyl and thiosulphuric acids. Moreover, sparingly soluble salts of divalent Pb are the chloride, bromide, iodide, fluoride, sulphate and carbonate. On the other hand, the Pb tetravalent ion is complexed by chloride in a concentrated HCl medium, and by sulphuric in a fairly concentrated medium (Pourbaix, 1966).

Metallic Pb exposed to air is first oxidised by oxygen to yield lead hydroxide, and later attacked by atmospheric CO_2 , generating thus a lead carbonate film which protects the metal against further corrosion. Lead is also transformed into sulphate, chloride and, generally, other very stable salts through reaction with sea or saline waters. However, these salts are attacked by acidic or very low salinity waters, later causing new corrosion processes in the metal.

The total Pb concentration in natural unpolluted waters ranges between 0.05 to 10 mg/l while the dissolved Pb does not

exceed 0.010 mg/l (Stumm and Morgan, 1980; WHO, 1986; *Standard Methods*, 1989; Morell and Hering, 1993). Higher concentrations could indicate water pollution by waste waters or sewages rich in the metal. The concentration of Pb in treated waters is much lower than that of the original raw untreated water.

Lead has been used historically as piping material in the networks of drinking-water systems and as a consequence, concentrations of Pb in drinking water can increase up to 2 mg/l , i.e. Scotland (WHO, 1986) in acidic and very low salinity waters. This justifies the substitution of Pb by other metals like Cu and Fe.

Lead is an element which is not physiologically essential, having conversely, a toxic character. In this sense, the acute toxicity of lead to freshwater organisms is greater in soft water than in hard water.

In the humans, the metal produces the "saturnism" disruption, a disease characterised by Pb accumulation in bones, and especially nervous, renal and hepatic systems. Saturnism causes anaemia, paralysis, headaches, and enzymatic and lipid tissue alterations. Moreover, Pb is also a typical carcinogenic element (Leed, 1972; García Garrido, 1986; WHO, 1986; Otero Gonzalez et al., 1989).

Like mercury, Pb is accumulated in the body and excreted very slowly. Thus, Pb can pass from mother to foetus across the placental system; in this case, Pb reacts with sulphur amino acids and then, causes difficulty in oxygen exchange in cells. In this way, correlations between mental retardation in children and high levels of Pb in blood have been proven.

All these evidences justify the decreasing use of Pb in the world since the early seventies (WHO, 1993; EUREAU, 1994). Likewise, both the World Health Organisation and the European Union have recently recommended or proposed to minimise the Pb level in drinking water (see Table 2).

Lithium

Atomic number 3

Symbol Li

Atomic mass 6,94

Oxidation number for dissolved substances:

+1(lithium ion).

Lithium is usually found as impurity of sodium and potassium minerals as well as in the form of fluoride and complex silicates. This alkali metal practically does not form any complexes, its salts being very soluble. The mean levels of Li in water do not usually exceed some $\mu g/l$ (Catalán Lafuente, 1981; *Standard Methods*, 1989; Morell and Hering, 1993) with the exception of waters coming from lithious wells.

Physiologically, the relation between cardiac illness and consumption of very poor Li waters (lower than 1 to 2 $\mu g/l$) has been investigated. On the other hand, ingestion of drinking waters with near 100 $\mu g/l$ of Li seems to decrease the above problems and therefore, the incidence of stomach ulcers (WHO, 1986).

Magnesium

Atomic number 12

Symbol Mg

Atomic mass 24,32

Oxidation number for dissolved substances:

+1(magnesium ion), +2(magnesium ion).

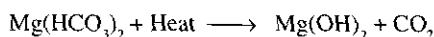
Magnesium is associated with the **hardness** of water, and thus, to Ca. It is present in the earth's crust as carbonates, sulphates and chlorides (Stumm and Morgan, 1980; Marín Galvín, 1995). Moreover, Mg is a frequent component of silicates associated with Al in this case.

Magnesium can form soluble complexes such as tartrate and metaphosphate, its salts being very soluble, except oxalate, carbonate, phosphate and fluoride (Pourbaix, 1966).

Saline waters can contain up to 30 g/l of Mg. Nevertheless, the mean concentrations in waters (not sea waters) range generally between 20 to 40 mg/l: this implies that Mg is the second most abundant metal in waters after Ca.

The amount of Mg changes along a river from the head to the outlet into the sea due to dissolution processes of rocks and minerals carried out by the river water. In this way, as example, the relative amount of Mg in the Ebro River (Spain) increases from around 18% of the dissolved salts near its head up to around 21% at its outlet into the Mediterranean sea (mean yearly values before 1980) (Catalán Lafuente, 1981).

From a point of view of water use, Mg is involved in a complex equilibrium between non-soluble carbonate and the more soluble bicarbonate (produced by reaction with atmospheric CO₂) similar to that mentioned of Ca. This dynamics can provoke undesirable **corrosion-precipitation** phenomena in the drinking-water system networks. Furthermore, when water is used for steam boilers, magnesium bicarbonate under heating can produce non-soluble magnesium hydroxide and CO₂, according to the general reaction:



The CO₂ generated in this process is undesirable because it can severely attack the boiler materials.

Physiologically, Mg is very important in the functioning of certain enzymatic systems as well as in the formation of bones. It has been proven that the ingestion of waters with <15 mg/l of Mg can be related to high rates of cardiac pathology. This effect has not been detected in communities which habitually ingest drinking water with more than 30 to 35 mg/l of magnesium. Finally, high rates of Mg (specially, sulphate) adds a bitter taste and cause laxative effects in consumers (USEPA, 1977).

Manganese

Atomic number 25
Symbol Mn
Atomic mass 54,93

Oxidation number for dissolved substances:

+2(manganous and dimanganite ions), +3(manganic ion), +5(manganite ion?), +6(manganate ion), +7(permanganate ion).

Manganese is widely diffused in nature. **Pyrolusite** (manganese dioxide) and sulphide are outstanding minerals. It can easily be dissolved by acid or neutral oxidising solutions with the formation of manganous ions. A slight oxidising action can oxidise the manganous solutions with the formation of solid oxides. Finally, a powerful oxidising action can oxidise these solutions to the hexavalent or heptavalent state.

Manganese gives rise in particular the following complexes: fluorine, phosphoric, oxalic and ammine-Mn²⁺ complexes; hydrochloric, phosphoric, sulphur, cyanide and oxalic-Mn³⁺

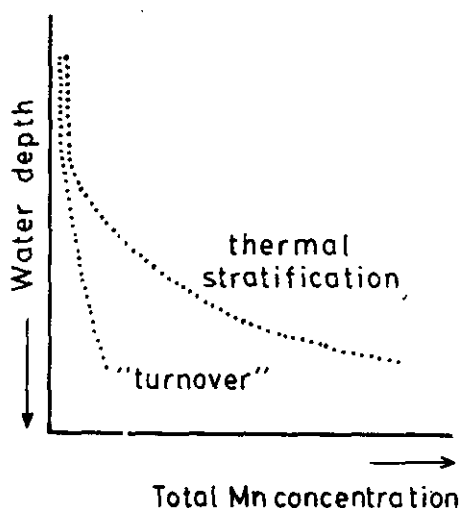


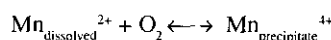
Figure 3
General depth dynamics for total Mn in a typical temperate zone reservoir

complexes; hydrochloric, hydrofluoric and cyanide-Mn²⁺ complexes (Pourbaix, 1966).

Manganese levels in well-oxygenated waters are low because the most soluble Mn compounds are the divalent ones; in an aerated water medium the oxidation of these latter occurs rapidly and, consequently, the precipitation of non-soluble Mn⁴⁺ compounds (WHO, 1986).

Manganese in waters is in dissolved, colloidal and complex forms. In this way, it is known the rapid formation of **Mn-organic matter** complexes which are very stable and cause major problems in water treatment processes for drinking water production. Generally, concentrations of Mn in natural waters range from very low μg/l to 0.5 mg/l (or even >1.0 mg/l) (Stumm and Morgan, 1980; Marín Galvín, 1995).

Nevertheless, underground waters rich in organic matter and poorly oxygenated, as well as anoxic deep waters of lakes and reservoirs in the thermal stratification period (see Fig. 3) may exceed the 2 to 3 mg/l of total Mn (Stumm and Morgan, 1980; Wetzel, 1981; Marín Galvín 1991b-c; Morel and Hering, 1993). This can be explained taking into account the complex redox dynamics experienced by the metal (similar to that of iron) globally summarised as follows:



This behaviour has been extensively studied in several cases (Stumm and Morgan, 1980; Morel and Hering, 1993). During the thermal mixing period of lakes ("turnover", winter-spring) the total Mn levels in all the water profile are homogeneous and low (waters well oxygenated) not increasing in the deep waters. During the stratification period (summer-autumn), especially in deep poorly oxygenated waters, the levels of Mn increase sharply due to the dissolution processes in reducing ambient from oxidised Mn compounds present in muds and sediments of a lake. Likewise, this phenomenon is also favoured by anaerobic micro-organisms (**manganese bacteria**) (Wetzel, 1981; Marín Galvín, 1995).

Manganese is an essential **trace element** being involved in the synthesis of flavo proteins, cholesterol dynamics and haemoglobin production. Mn is also a known enzymatic catalyst. On the other hand, Mn deficiency in the body is associated with heart disease,

anaemia and bone malformation in children. Furthermore, habitual ingestion of waters rich in Mn (14 mg/l) will cause brain illnesses. Fortunately, Mn does not seem to have a carcinogenic incidence (Leed, 1972; USEPA, 1977).

With respect to drinking-water consumption, low levels of Mn can provoke the appearance of manganese bacteria in network systems as well as colouring and turbidity (Degrémont, 1979; Tchobonaglou and Schroeder, 1985; Marín Galvín, 1995). Thus, more than 0.2 mg/l of Mn produce bad tastes (Zoeteman, 1980). This implies the necessity of totally removing the metal during the treatment of raw water to produce drinking water by using strong oxidation processes (Marín Galvín and Rodríguez Mellado, 1993), e.g. KMnO_4 is widely employed to reduce organics in raw water, taste and even dissolved Mn^{2+} .

Mercury

Atomic number 80
Symbol Hg
Atomic mass 200.61

Oxidation number for dissolved substances:

+1(mercurous ion), +2(mercuric and mercurate ions).

Mercury usually occurs in the earth's crust as the sulphide while at the same time being found in some mines as the liquid. The main sources of Hg in the environment are natural volcanic emissions followed by effluents rich in Hg discharged by certain industries, cement production, fuel combustion, batteries, sodium hydroxide and chlorine production. Moreover, Hg can also be used in pesticide formulations.

The following compounds of monovalent mercury are sparingly soluble: the halide, the chromate and the sulphide. Divalent mercury forms the following sparingly soluble compounds: iodide, thiocyanic and sulphide. Moreover, Hg^{2+} forms a large number of complexes which are often quite stable: chloride, hydrobromic, hydroiodic, thiocyanic, hydrocyanic, amine, sulphurous and thiosulphuric complexes (Pourbaix, 1966). On the other hand, Hg levels in waters are generally very low not exceeding more than 1 $\mu\text{g/l}$ (USEPA, 1977; Catalán Lafuente, 1981; García Garrido, 1986). However, in highly polluted waters in Germany, up to 0.40 mg/l have been detected in a few cases only (WHO, 1986).

Mercury is a typical element which experiences biotransformation processes in the environment (Leed, 1972; USEPA, 1977; ECC, 1979; *Standard Methods*, 1989) which increases its toxic potential. In this way, Hg in waters is found both in inorganic form as Hg^+ chloride and hydroxide, and in organic compounds such as the very toxic methyl, dimethyl and phenyl. Likewise, some Hg^{2+} inorganic compounds can be detected in waters as HgCl_2^{2+} (WHO, 1990c-d).

Oxidation of Hg^+ compounds in well-oxygenated waters and especially those with pH lower than 5.0 is rapid, yielding Hg^{2+} . Later, Hg^{2+} can react according to two processes:

- Reduction to metallic Hg carried out by *Pseudomonas* and other water micro-organisms. Once Hg is formed, it might be evaporated to the atmosphere, and later, it is deposited in rain.
- Formation of very toxic **organo-mercury** compounds such as methyl mercury and dimethyl mercury. In this way, Hg^{2+} is either associated with organic particles, or with microorganisms, or even with the bottom sediments of natural water systems, experiencing a process of **methylation** in both oxygenated and anoxic media.

In the oxygenated medium, the process yields firstly mercuric methionin which later breaks down to produce methyl derivatives. If the pH of water is low, the formation of methyl mercury is favoured against dimethyl mercury.

Mercury and its derivatives are very toxic, being rapidly adsorbed by organisms. Due to its slow kinetics of elimination, mercury exhibits bioaccumulation phenomena in the trophic chain. The higher the organism the higher the amount of Hg in the animal's body.

This phenomenon was clearly demonstrated in the town of Minamata, Japan (García Garrido, 1986; WHO, 1986): Mercury emanating from the industrial waste waters of an industry near the town was initially accumulated by phytoplankton, secondly by zooplankton, later by fish, and finally, by humans who ate the mercury-polluted fish. Thus, the levels of mercury in humans were much higher than those of the original waste-water emissions.

Adsorption of organic mercury into the body is about 90 to 95% of that ingested, whereas only about 10% of inorganic mercury is adsorbed. Hg accumulates in fatty tissues, brain, renal system, muscles, bones and nervous system, with a tendency to cause muscle paralysis, visual disruptions and brain damage.

Mercury causes moreover alteration of enzymes involved in the circulatory system. Finally, the result could be teratogenesis because it can alter the chromosome division process.

Molybdenum

Atomic number 42
Symbol Mo
Atomic mass 95.94

Oxidation number for dissolved substance:

+3(molybdenous ion), +6(molybdate and acid molybdate ions), +7(permolybdate and condensed molybdenum ions)

Molybdenum bromide, chloride and sulphide are sparingly soluble, as are the molybdates of the majority of metals other than the alkali metals. Molybdenum forms also a large number of complexes: hydrochloric, oxalic, thiocyanic complexes of Mo^{3+} ; hydrochloric, hydrofluoric, phosphoric, arsenic, vanadic, citric, tartaric and oxalic complexes of Mo^{6+} (Pourbaix, 1966).

Concentrations of Mo found in natural waters are very low ranging around 0.05 mg/l or less. Nevertheless, in areas near mining operations these levels can increase up to 0.20 mg/l (WHO, 1993). With respect to drinking waters, Mo concentrations do not usually exceed 0.01 mg/l.

This metal is considered to be an essential element being involved in the structure of oxydases which metabolise xantine, aldehydes and sulphites. To date, toxic effects of Mo in humans have not been demonstrated.

Nickel

Atomic number 28
Symbol Ni
Atomic mass 58.69

Oxidation number for dissolved substances:

+2(nickelous, nickelite and dinickelite ions), +3(nickelic ion), +6(nickelate ion).

Nickel is naturally found as the arsenate and sulphide. This metal is used in the melting process of metallic alloys, as catalyst and in pesticide formulations.

Nickel salts are reasonably soluble in water, except the ferri- and ferrocyanides, sulphide and Ni-dimethylglyoxime. Likewise, the existence of the following complexes of Ni is known: hydrochloric, and sulphuric (very stable), amine (fairly stable), oxalic, thiocyanide, metaphosphoric, pyrophosphoric and cyanide complexes (Pourbaix, 1966).

The main levels of Ni in surface waters do not generally exceed 5 to 10 $\mu\text{g}/\text{l}$; however, they can exceed 1 mg/l . Conversely, in underground waters of Russia up to 13 mg/l of Ni have been tested (Sidorenko and Itskova, 1980). On the other hand, Ni in drinking water shows a level lower than 20 $\mu\text{g}/\text{l}$ with exceptions. In certain cases where waters are distributed by Ni pipe networks, these levels have strongly deteriorated.

Nickel is not generally very toxic; however, certain salts can have potentially carcinogenic and mutagenic effects according to laboratory investigations (USEPA, 1977; ECC, 1979; WHO, 1986). This is explained by the reaction between the metal and cellular DNA. Finally, high ingestion of Ni can cause renal problems and skin allergies by contact (WHO, 1990e).

Potassium

Atomic number 19
Symbol K
Atomic mass 39.10
Oxidation number for dissolved substances:
+1(potassium ion).

Potassium is widely dispersed in nature as the chloride, sulphate, fluoride and phosphate, as well as in mineral clays. In the latter, this metal appears as the typical natural radioisotope ^{40}K which contributes to the background radiation of the earth's crust (UN, 1988; *Standard Methods*, 1989; Marín Galvín, 1995).

Like all alkaline metals, K salts are very soluble. This metal forms practically no complexes.

Industrial sources of K to the environment are especially agricultural fertilisers as well as certain industries, like sugar production from beets.

Potassium is generally the fourth most common metallic element present in water (after Ca, Mg and Na), usually not exceeding 15 mg/l . Sea waters show higher K concentrations than fresh waters.

Evolution of K along a river experiences a decreasing trend while that of Na increases: this is due to the possibility of K substituting Na in clay mineral layers. This also implies that the ratio (**sodium/potassium**) decreases between a river source and its mouth.

On the other hand, K levels in industrial waters used for heat exchangers must be reduced because they cause very important corrosion effects.

Physiologically, deficiency of K in organisms is associated with disruptions of nervous and muscle systems. This element is usually not toxic for humans via the oral route but clearly essential.

Selenium

Atomic number 34
Symbol Se
Atomic mass 78.96
Oxidation number for dissolved substances:
-2(selenide and hydrogen selenide ions), +4(selenite and acid selenite ions, selenious acid), +6(selenate and acid selenate ions, selenic acid), +7(perdiselenic acid).

Selenium is an essential element being widely spread in nature, especially in volcanic zones, but in small amounts; it is associated with Cu, S and F.

From a chemical point of view, the selenides, selenites and selenates of metals other than the alkali metals are generally insoluble; moreover, Se forms complexes such as selenophosphoric acid $\text{PS}:(\text{OH})_3$, chromoselenite acid, cobaltiselenic complexes and complexes derivatives of uranic acid and nitrosylsulphuric acid.

Concentrations of this element in surface waters as SeO_3^- (selenite), SeO_4^{2-} (selenate) and dimethyl selenium typically do not exceed 10 $\mu\text{g}/\text{l}$ (WHO, 1993). Underground waters, conversely, can contain up to 1 mg/l , especially in waters which drain volcanic land; as for example, in certain zones of the USA (Catalán Lafuente, 1981; WHO, 1986).

Furthermore, a recent study carried out in the USA (Liu and Narasimhan, 1994) demonstrated that Se exhibits a trend in depth in lakes and reservoirs, similar to Al, Fe and Mn; this is due to chemical, electrochemical and microbiological factors.

From a physiological point of view Se is an essential element being integrated into certain enzymes and amino acids as selenium methionine and selenium cysteine. Likewise, Se is involved in the **factor-3**, essential for animal nutrition.

The detoxifying power of Se against other toxic metals such as Cd is known. Deficiency of Se in human nutrition causes **Keshan** disease, categorised by cardiac pathology (USEPA, 1977). At the same time, a certain anticarcinogenic effect of Se in *in vivo* laboratory studies appears to have been demonstrated elsewhere (Jacobs, 1980).

On the other hand, excessive ingestion of Se might produce skin lesions, nervous and intestinal problems and appearance of dental caries. Finally, presence of As in drinking water may increase the potential toxicity of Se.

Silver

Atomic number 47
Symbol Ag
Atomic mass 107.89
Oxidation number for dissolved substances:
+1(argentous and argentite ions), +2(argentic ion),
+3(argentyl ion).

Silver is relatively rare in nature, forming 0.1 mg/kg of the earth's crust. Silver is found mainly as the mineral **argentite** and associated likewise with Pb, Zn, Cu and Au salts (WHO, 1986; *Standard Methods*, 1989).

The Ag compounds are widely used by man in solder, photography, electric equipment, electrolytic processes, pesticides, jewellery, dental prostheses and pharmaceutical products.

Silver forms a large number of complexes, some of which are very stable, e.g. the thiosulphuric and cyanide complexes. Almost all silver salts are sparingly soluble; the nitrate, perchlorate, fluoride, acetate and chlorate are soluble.

The Ag levels in waters are in the very low range, between 1 to 10 $\mu\text{g}/\text{l}$, with the exception of waste waters discharged by certain industries (Degrémont, 1979; García Garrido, 1986).

Silver salts have been used in water treatment and in domestic filters due to their bactericidal action. In such processes up to 50 $\mu\text{g}/\text{l}$ Ag can be detected in drinking water.

This metal is not especially toxic to humans, provided ingestion

is moderate. On the other hand, small but continued doses can cause a disease named **argiria**, in which the afflicted individual develops a blue colouration in the skin due to deposition of metallic Ag in the dermis and pilose follicles, as well as in the sebaceous and sudoriferous glands. Higher ingestion of the metal can be deposited in the liver, renal and respiratory systems and cornea (USEPA, 1977; WHO, 1986). Finally, the possible carcinogenic effect of Ag has not been demonstrated to date.

Sodium

Atomic number 11
Symbol Na
Atomic mass 22.99

Oxidation number for dissolved substances:
 +1(sodium ion).

Sodium is an element commonly found as salts (chloride, sulphate) and in silicates and clay minerals. Like the lithium and potassium alkali metals, all the Na salts are very soluble and there are practically unknown complexes of sodium.

The use of Na compounds by man is widespread: salting industries, pulp and paper production, pharmaceutical products, electrolytic processes, water treatment and, even, to spread NaCl on the roads to facilitate snow-ice removal. All these activities are potential sources of Na to the environment, as well as human defaecation and the substitution of Na by K in the clay minerals as stated above (see **potassium**).

Due to the high solubility of Na salts, the occurrence of Na in waters is high being the third or, perhaps even, the second major element found in continental waters (up to 300 mg/l) and the first in sea waters (about 10 g/l) (Stumm and Morgan, 1980; Morel and Hering, 1993). The presence of Na salts in drinking waters causes a salty taste. This phenomenon is also associated with water temperature and specific salts; thus, the following perception thresholds have been established for different Na salts: 20 mg/l for Na₂CO₃, 150 mg/l for NaCl, 190 mg/l for NaNO₃, 220 mg/l for Na₂SO₄ and 420 mg/l for NaHCO₃ (Marín Galvín, 1995).

Physiologically, high levels of Na in blood will result in heart problems, like hypertension, renal and liver pathology and intoxication in pregnancies and babies (Catalán Lafuente, 1981).

Tin

Atomic number 50
Symbol Sn
Atomic mass 118.69

Oxidation number for dissolved substances:
 +2(stannous, stannyl, stannite and bismannite ions),
 +4(stannic, stannate and acid stannate ions),
 +7(perstannate ion).

Compounds of Sn in nature are found infrequently, being especially associated with salts of other more abundant metals such as Pb and Zn.

Divalent Sn forms the following complexes: SnCl⁺, SnCl₂, SnCl₄⁼ and very stable oxalic complexes; tetravalent Sn forms SnCl₂⁺⁺, SnCl₃⁺, SnCl₅⁻; SnCl₆⁼ and oxalic, hydrofluoric and sulphydric complexes. Finally, stannous and stannic sulphides are sparingly soluble (Pourbaix, 1966).

Because of the natural dissolution of tin minerals, another

source of Sn to waters is the use of pesticides which contain the metal in its formulation to eliminate snails. However, these organic Sn compounds are easily degraded through photochemical and biological processes in nature.

Due to the low occurrence and solubility of Sn compounds, natural waters only contain low concentrations of Sn: usually <10 µg/l. In drinking waters the levels commonly do not exceed 1 to 2 µg/l (WHO, 1993). Nevertheless, the increasing use of Sn in solder in domestic water pipes can cause an increase of the metal in drinking water.

Tin as well as inorganic Sn compounds are poorly absorbed from the gastrointestinal tract, being rapidly excreted and not accumulated in tissues. According to the available evidence (Leed, 1972; USEPA, 1977; ECC, 1979; WHO, 1993) this metal has not been shown to be teratogenic or embryotoxic in *in vivo* laboratory studies. Excessive levels of Sn in foods can cause acute gastric irritation.

Zinc

Atomic number 30
Symbol Zn
Atomic mass 65.38

Oxidation number for dissolved substances:
 +2(zincic, zincyl, zincate and bizincate ions).

This element occurs frequently in nature, being generally associated with Fe, Cu, Cd and Pb sulphides, and found in particularly ZnS (**blende**).

Zinc forms the following complexes: amine, cyanide, thiocyanide, oxalic and hydrochloric complexes, and others with ethylene diamine, pyridine, aniline and hydrazine. There is a large number of sparingly soluble Zn compounds, including the following: blende, zinc cobaltcyanide, ammonia-zinc phosphate, the iodate and ZnCO₃ (Pourbaix, 1966).

Zinc is commonly used by man as an antirust agent, in the galvanising industry, for paint production and in the textile industry. The concentration of Zn in waters is usually low, being detected as inorganic, ionic or colloidal compounds. The more frequent species in water are Zn²⁺, Zn(OH)⁺ and ZnCl₃⁻. In this way, the mean values of Zn in surface waters are lower than 10 µg/l, while in underground waters they do not commonly exceed 50 µg/l (WHO, 1993).

Likewise, ZnCl₂ and ZnSO₄ present in waters react with dissolved CO₂ yielding hydroxides and carbonates which are strongly adsorbed onto sediments and muds of the river beds or lakes. This fact explains the low levels found in waters.

Occasional presence of Zn in drinking waters (>50 µg/l) is due to partial solubilisation of pipeline coatings used in the distribution network. Nevertheless, this phenomenon is very unusual.

Zinc is an essential element for life (Sola and Durán, 1994). In this sense, it is present in several amino acids as Zn-cysteine and Zn-histidine and numerous enzymes such as alcohol dehydrogenase, carboxy peptidase and carbonic anhydrase (Gray and Bertini, 1986), involved, respectively in ethanol and protein metabolism. Zinc is also contained in alkaline phosphatase and superoxide dismutase enzymes. Due to this, Zn has a great influence on human growth, encephalic development, reproduction, the immunological system and on correct cellular metabolism. Moreover, this metal acts as an insulin co-factor in glucose metabolism (Gray and Bertini, 1986).

Finally, Zn is considered by many authors as to be a non-toxic metal (García Garrido, 1986; WHO, 1986) even in high doses. However, increases of Zn in drinking water are generally associated with those of toxic Cd. This reality should alert Water Authorities with respect to the consumption of waters relatively rich in Zn, and potentially rich in Cd.

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References

- BRENNIMAN GR, KOJOLA WH, LEVY PS, CARNOW BW and NAMEKATA T (1979) Health effects of humans exposure to barium in drinking water. *Gov. Rep. Announce. Index.* (U.S.) **79** 80-86.
- CATALÁN LAFUENTE J (1981) *Química del Agua*. Alonso Ed., Madrid (Spain).
- DEGRÉMONT (1979) *Manual Técnico del Agua* (4th edn.). Bilbao (Spain).
- DRISCOLL CT (1985) Aluminium in acidic surface waters: chemistry, transport and effects. *Environ. Health Perspect.* **63** 93-99.
- DUTTA A AND CHAUDHURI M (1991) Removal of arsenic from groundwater by lime softening with powdered coal additive. *J. Water-SRT Aqua* **40** (1) 25-29.
- ECC (EUROPEAN COMMUNITY COUNCIL) (1979) *Trace metals: Exposure and Health Effects*. Pergamon Press, Oxford (England).
- EU (EUROPEAN UNION) (1995) Proposal for a council directive concerning the quality of drinking waters. *Official Journal* **95/C 131**, Brussels.
- EUREAU (1994) Implications to water suppliers and householders of the new WHO guidelines for drinking water quality. *J. Water SRT-Aqua* **43** (6) 315-322.
- GARCÍA GARRIDO J (1986) *El Agua en la Producción*. Prensa XXI S.A. Ed., Barcelona (Spain).
- GRAY H and BERTINI I (1986) *Progress in Inorganic Biochemistry and Biophysics, Vol. 1. Zinc Enzymes*. Birkhäuser Boston Inc. Ed. Boston (USA).
- GRUNDL T and DELWICHE J (1993) Kinetics of ferric oxyhydroxide precipitation. *J. Contaminant Hydrol.* **14** 71-97.
- HEMM JD (1986) Geochemistry and aqueous chemistry of aluminium. *Kidney Int.* **29** (18) S3-S7.
- HIAT V and JUFF JE (1975) The environmental impact of cadmium: An overview. *Int. J. Environ. Studies* **7** 277-290.
- JACOBS MM (1980) Effects of selenium on chemical carcinogens. *Preventive Medicine* **9** 362-367.
- LEED DHK (1972) *Metallic Contaminants and Human Health*. Academic Press Ed. New York (USA).
- LIU CHW and NARASIMHANTN (1994) Modeling of selenium transport at the Kesterson reservoir, California, USA. *J. Contaminant Hydrol.* **15** 345-366.
- MARÍN GALVÍN R (1981) Graduation Thesis. Universidad de Córdoba (Córdoba, Spain).
- MARÍN GALVÍN R (1991a) Study of evolution of aluminium in reservoirs and lakes. *Water Res.* **25** (12) 1465-1470.
- MARÍN GALVÍN R (1991b) Evolución del contenido en Aluminio en el embalse de Guadalmeñato. *Tecnología del Agua* **78** 17-23.
- MARÍN GALVÍN R (1991c) Evolución del contenido en Aluminio en el embalse de Guadalupe. *Equipamientos y Servicios Municipales* **39** 57-63.
- MARÍN GALVÍN R (1995) *Análisis de Aguas y Ensayos de Tratamiento: Principios y Aplicaciones*. GPE, SA Ed. Barcelona (Spain).
- MARÍN GALVÍN R and RODRÍGUEZ MELLADO JM (1993) A note on the use of chlorine dioxide vs. chlorine for potable water treatment. *Water SA* **19** (3) 2: 1-234.
- MOREL FMM and HIRING JG (1993) *Principles and Applications of Aquatic Chemistry*. Wiley and Sons Inc., New York (USA).
- MULLEN ED and RITTER JA (1974) Potable-water corrosion control. *J. AWWA* **66**, 473-479.
- NEAL C (1994) Aluminium speciation variations in an acidic upland stream draining the Hafren spruce forest, Plynlimon, Mid-Wales. *J. Hydrol.* **164** 39-51.
- OTERO GONZALEZ A, MORA BERMUDEZ B, CAO GONZALEZ M and RODRIGUEZ, MIGUEZ L (1989) Epidemiología de la intoxicación por plomo de agua domiciliaria y saturnismo. Valoración de parámetros para el estudio de grandes poblaciones. *Tecnología del Agua* **62** 47-56.
- POURBAIX M (1966) *Atlas of Electrochemical Equilibria*. Pergamon Press Ed. Oxford (England).
- SOLA M and DURÁN M (1994) El zinc y los enzimas: Importancia y estudio mediante modelos. *Química e Industria* **42** (7) 24-28.
- SIDORENKO GI and ITSKOVA AI (1980) *Niquel*. Medica Ed., Moscú (Russia).
- STANDARD METHODS (1989) *Standard Methods for the Examination of Water and Wastewater* (17th edn.). APHA, Washington DC (USA).
- STUMM W and MORGAN JJ (1980) *Aquatic Chemistry*. Wiley Interscience, New York (USA).
- SUET-MEI H and WING-SHIU T (1992) Sanitary and health aspects of aluminium in drinking water. Paper presented at the IWSA International Workshop on Aluminium in Drinking Water (January 15-17). Hong Kong.
- TCHOBONAGLOUS G and SCHROEDER ED (1985) *Water Quality*. Addison-Wesley Pub. Co. Ed., Reading (Mass.-USA).
- TRAPP GA (1986) Interactions of aluminium with cofactors, enzymes, and other proteins. *Kidney Int.* **29** (18) S12-S16.
- UN (United Nations) (1988) *Scientific Committee on the Effects of Atomic Radiations: Sources, Effects and Risks of Ionizing Radiation*. New York (USA).
- UNDERWOOD EJ (1977) *Trace Elements in Human and Animal Nutrition*. Academic Press Ed. New York (USA).
- USEPA (US Environmental Protection Agency) (1977) *Toxicology of Metals, Vol. II*. Washington DC (USA).
- USEPA (US Environmental Protection Agency) (1980) *Ambient Water Quality Criteria for Beryllium*. Washington DC (USA).
- WETZEL RG (1981) *Limnología* (Spanish edn.). Omega, S.A. Ed. Barcelona (Spain).
- WHO (World Health Organization) (1981) *Critères d'hygiène de l'environnement* 18. Geneve (Switzerland).
- WHO (World Health Organization) (1986) *Directives de Qualité pour l'eau du Boisson*, Vol. I, II y III. Geneve (Switzerland).
- WHO (World Health Organization) (1990a) *Environmental Criteria Health Series (no 107): Barium*. Geneve (Switzerland).
- WHO (World Health Organization) (1990b) *Environmental Criteria Health Series (no 106): Beryllium*. Geneve (Switzerland).
- WHO (World Health Organization) (1990c) *Environmental Criteria Health Series (no 118): Inorganic Mercury*. Geneve (Switzerland).
- WHO (World Health Organization) (1990d) *Environmental Criteria Health Series (no 101): Methylmercury*. Geneve (Switzerland).
- WHO (World Health Organization) (1990e) *Environmental Criteria Health Series (no 108): Nickel*. Geneve (Switzerland).
- WHO (World Health Organization) (1992) *Environmental Criteria Health Series (no 134): Cadmium*. Geneve (Switzerland).
- WHO (World Health Organization) (1993) *Guidelines for Drinking Water Quality* (2nd edn.), Vol. I. Geneve (Switzerland).
- ZOETEMAN BCJ (1980) *Sensory Assessment of Water Quality*. Pergamon Press Ed. Oxford (England).