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HEAVY METALS AS TRACE CONSTITUENTS IN NATURAL GROUNDWATERS AND POLLUTED

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SUMMARY

The natural and man-made concentrations of heavy metals are discussed concerning their abundance, geochemical mobility and their physiological effects on man. The many gaps of geochemical information concerning abundance and behaviour of heavy elements in the ground should be filled especially for those elements which are important to human health.

INTRODUCTION

Heavy metals are usually defined as metals with densities larger than 5 g . cm^{-3}. This group includes 67 elements with the atomic numbers 23-32, 40-51, 57-84 and 87-103. The heavy metals with the atomic numbers 61 and 93-103 are artificial elements.

The element technetium (atomic number 43) was found in a sample of molybdenum which had been bombarded with neutrons in the Berkeley Cyclotron. The search for this element in terrestrial materials was without success so far, but it has been reported from the spectra of stars (C o r r e n s, 1969).

If heavy metals in groundwater are to be discussed, there are two aspects under which those elements can be chosen. The first one is their abundance in groundwater, the second one is their importance for human health either in a beneficial or a noxious sense.

As far as the abundance of heavy metals in groundwater is concerned, only very little information is available except for those elements which influence the aptitude of groundwater for drinking, agricultural or industrial purposes or which are of interest as raw materials. Thus health effects are involved in the first aspect as well. The aspect of health effects has lifted some heavy elements, especially cadmium and mercury, into public interest since the recent poisoning of man in highly industrialized environments in Japan. For the most important heavy metals maximum permissible concentrations in drinking water are fixed.

Actually the sparsity of data and the hygienic importance of selected heavy metals decreases the number of interesting elements to some 22 species.

ABUNDANCE

The importance of any heavy metal in a natural groundwater is a result of its abundance in the earth crust and its geochemical mobility. Table 1 gives an idea of the natural abundances, showing the concentrations of the elements in magmatites as their primary source. Their mobility may be derived from the proportional decrease or increase in the products of weathering, in the resistates (sandstones), in the hydrolysates (shales), in the precipitates (carbonate and sulfate rocks), in the evaporites (salt deposits), and lastly in the sea water. The very low concentrations of the heavy elements in sea water as compared to their abundance in the primary rocks show their poor geochemical mobility resulting from low solubilities, from adsorption and ion exchange effects on minerals or organic materials, e.g. clay or humic substances, from precipitation and coprecipitation and from the fixation in biological material or in newly formed mineral substances.

D a v i s & d e W i e s t (1967) suggested the following classification of dissolved constituents referring to their abundance in water

major constituents	(1.0 - 1000 ppm)
secondary constituents	(0.01 - 10.0 ppm)
minor constituents	(1 ppb - 0.1 ppm)
trace constituents	(generally less than 1 ppb)

Using this classification the heavy metals are distributed in the two last groups, which may be designated as trace elements for the purpose of this paper. Only iron and manganese are more often found in concentration ranges of the group of the secondary constituents.

A special group are the radioactive heavy metals. The most important radionuclides belong to the radioactive series of the uranium-radium-series with 14 daughter-substances and the thorium-series with 10 daughter-substances. Sometimes the radioactive mother- and daughter-substances equilibrate in groundwater. The equilibrium should be established

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TABLE 1
Abundance of heavy elements in rocks (1) and seawater (2) (ppm) (H o r n & A d a m s, 1966 and H e m 1970 (1); T u r e k i a n, 1969 (2)).

Element	magmatites	sandstones	shales	precipitates	evaporites	seawater
Ag	0.151	0.122	0.271	0.189	–	$2.8.10^{-4}$
Bi	–	–	–	–	–	$2 .10^{-5}$
Cd	0.192	0.0199	0.0476	–	–	$1.1.10^{-4}$
Co	23	0.328	8.06	0.123	1.6	$3.9.10^{-4}$
Cr	198	120	423	7.08	10.6	$2 .10^{-4}$
Cu	97.4	15.4	44.7	4.44	2	$9.1.10^{-7}$
Fe	42200	18600	38800	8190	265	$3.4.10^{-3}$
Ga	18.5	5.87	22.8	2.69	–	$3 .10^{-5}$
Ge	1.39	0.881	1.32	0.363	–	$6 .10^{-5}$
Hg	0.328	0.0574	0.272	0.0456	–	$1.5.10^{-4}$
Mn	937	392	573	842	4.4	$4 .10^{-4}$
Mo	1.25	0.50	4.25	0.75	1.5	$1 .10^{-2}$
Pb	15.6	13.5	80	16.5	0.9	$3 .10^{-5}$
Ra	–	–	–	–	–	$1 .10^{-10}$
Ru	–	–	–	–	–	$7 .10^{-7}$
Sb	0.509	0.0138	0.808	0.200	–	$3.3.10^{-4}$
Sn	2.49	0.115	4.12	0.166	–	$8.1.10^{-4}$
Tl	1.1	1.5	1.6	0.065	–	–
U	2.75	1.01	4.49	2.2	0.2	$3.3.10^{-3}$
V	149	20.3	101	12.6	0.3	$1.9.10^{-3}$
W	1.42	1.56	1.92	0.561	–	$<1 .10^{-6}$
Zn	80	16.3	130	15.6	0.6	$5 .10^{-3}$

after the time ten times as long as the respective half-life of the daughter elements. Radioactive disequilibria are found in those cases where the flow rate of groundwater is high relative to the respective half-life of the radionuclide. Another reason may be any process which removes the daughter products from solution, e.g. each of the two above mentioned decay series yield in their midst a gaseous daughter product, the radon with a half-life of 3.8 days and the thoron with a half-life of 54 seconds. Both gases may escape to the atmosphere and to the surface water thus disturbing the radioactive equilibrium.

The natural background content of heavy metals has to be considered when human influence of local or regional scale are discussed. Therefore the available data from natural groundwater are arranged in the following preliminary list (table 2). The values are classified into the groups fresh groundwater, mineral water including oil field brines, thermal water, groundwater in mineralized zones and mine waters. The table shows many gaps of information.

Furthermore exact statistical criteria are missing for the fixation of the background concentration in normal fresh groundwater. This dilemma shows up for example in the surprising high amounts of heavy metals in some groundwater in the Netherlands (B r i n k m a n, 1974; E n g e l e n, 1974).

SOLUBILITY

The solubility of the heavy metals is generally controlled by the most abundant anions in natural groundwater. These are hydroxide, hydrogencarbonate, carbonate, sulfate, chloride, nitrate and – in a reducing environment – sulfide. Therefore the mobility of the heavy metals depends on the solubility of their hydroxides, carbonates, sulfates, chlorides and sulfides. Some of them are listed in table 3 in comparison with the poorly soluble bariumsulfate.

The solubility of some elements, for example the mobility of iron, is very strongly influenced by the pH and Eh of the groundwater. Generally ferrous compounds are more soluble than the corresponding ferric compounds, e.g. at pH 7 ($a_{OH^-} = 10^{-7}$) the activity of $Fe^{2+} = 10^{-1}$ indicates a much higher solubility of $Fe(OH)_2$ than that of the $Fe(OH)_3$, whose activity equals 10^{-16}. Eh-pH-diagrams as published by H e m (1970) and G a r r e l s & C h r i s t (1965) are useful qualitative and comprehensive guides to understand the relations between the solid and dissolved species even if they cannot be used as quantitative descriptions. One of the reasons for this restriction is the forming of soluble complexes with dissolved organic materials. In a similar way the

TABLE 2
Preliminary list of heavy metal concentrations in natural groundwaters.

element	fresh groundwater	mineral water oilfield brines	thermal water	groundwater in mineralized zones	mine waters
Cd	<10 ppb	5-71 ppb (California) (1)	–	up to 207 ppb (2)	up to 41,1 ppm St. Lawrence mine (3)
Cr	< 1 ppb	up to 21 ppb (California) (1)	–	–	–
Co	< 1 ppb	–	–	20 ppb (average S-Ural) (4)	–
Cu	<10 ppb	up to 344 ppb (Germany, USSR) (5), (6)	–	200 ppb (average S-Ural) (4)	up to 45 633 ppm, Mountain View mine, Butte, Montana (3)
Fe	<0,01-10 ppm	up to 1000 ppm (4)	–	–	up to 474,6 ppm, Alabama Coon mine, Joplin County Missouri (3)
Hg	∿0,03 ppb (7)	–	–	–	–
Mn	≪ 1 ppm	up to 30 ppm (8)	up to 42 ppm (Japan) (8)	–	up to 841 ppm, Comstock Lode, Storey County (8)
Mo	up to 3 ppb	–	up to 10 ppm (Japan, USSR) (9) (10)	–	–
Ni	< 4 ppm	up to 40 ppm (5)	–	40 ppb (average S-Ural) (4)	up to 319 ppm, Wolf mine Herford, Siegerland (11)
Pb	<10 ppb	up to 380 ppb (5, 12)	–	up to 1300 ppm (13)	–
Ra	< 1 pCi/1	up to 720 pCi/1 (4)	up to 70000 pCi/1 (Japan, Austria, Germany) (15)	up to 100 pCi/1 (14)	–
Sb	up to 0,2 ppb	–	up to 0,930 ppb (USA, USSR, Japan, New Zealand) (16)	–	–
Sn	< 1 ppb	up to 670 ppb (Bulgaria, Harz) (17)	up to 1 ppb (Japan) (17)	–	–
U	<0,01-10 ppb	–	–	up to 460 ppb (18)	–
W	< 1 ppb	–	–	up to 64 ppm (USSR, USA) (19)	–
Zn	<10 ppb	up to 27.5 ppm (Canada, USA) (20)	0,5-5000 ppb average 192 ppb (Japan) (20)	up to 177 ppm (21)	up to 2412 ppm Alabama Coon mine, Joplin County, Missouri (3)

(1) Silvey 1967, (2) Udodov & Parilov 1961, (3) Smirnow 1954, (4) Hem 1970, (5) Krejci-Graf 1963, (6) Fricke & Werner 1957, (7) Haberer & Norman 1971, (8) White et al. 1963, (9) Sugawara et al. 1961, (10) Vinogradov 1957, (11) Heyl 1954, (12) Herrmann 1961, (13) Nowack & Preul 1971, (14) Scott & Barker 1961, 1962, Emrich & Lucas 1963, (15) Haberer 1969, (16) Onishi 1970, (17) Hamaguchi & Kuroda 1970, (18) Rogers & Adams 1970, (19) Krauskopf 1970, (20) Wedepohl 1972, (21) van Everdingen 1970.

mobility of manganese, cadmium, copper, mercury, vanadium, uranium and many other heavy elements is affected by the Eh and pH of groundwater.

PRECIPITATION AND COPRECIPITATION

Processes which change the chemical properties of a natural groundwater, e.g. its temperature, Eh or pH or the admixture of other groundwater with different dissolved constituents may give rise to the precipitation of some compounds when the solution becomes saturated. In the precipitates some foreign ions are commonly trapped in or substituted within the structure of the newly formed substances. This process, the so called coprecipitation, is very effective in removing trace elements, e.g. copper, lead, zinc, tungsten and vanadium, when ferric hydroxide and manganese hydroxide are precipitated. Radium is coprecipitated when barite is formed.

The importance of precipitation and coprecipitation for the mobility of heavy metals is obvious in such areas where Eh and pH of the groundwater changes on its flowpath. This

TABLE 3
Solubility products of different heavy metals and of $BaSO_4$.
(D'ans & Lax 1967 (1), Haberer 1969 (2), Hamaguchi & Kuroda 1970 (3).

	[mol/l]		(at 25°C)		
$BaSO_4$	$[Ba^{2+}]$	$[SO_4^{2-}]$	$1.08 \cdot 10^{-10}$		(1)
$CuCO_3$	$[Cu^{2+}]$	$[CO_3^{2-}]$	$1.37 \cdot 10^{-10}$		(1)
AgCl	$[Ag^{+}]$	$[Cl^{-}]$	$1.7 \cdot 10^{-10}$		(2)
$FeCO_3$	$[Fe^{2+}]$	$[CO_3^{2-}]$	$2.11 \cdot 10^{-11}$		(2)
$RaSO_4$	$[Ra^{2+}]$	$[SO_4^{2-}]$	$4.25 \cdot 10^{-11}$	(20°C)	(1)
$ZnCO_3$	$[Zn^{2+}]$	$[CO_3^{2-}]$	$6 \cdot 10^{-11}$		(1)
$PbCO_3$	$[Pb^{2+}]$	$[CO_3^{2-}]$	$1.5 \cdot 10^{-13}$		(2)
$Ni(OH)^2$	$[Ni^{2+}]$	$[OH^{-}]^2$	$1.6 \cdot 10^{-14}$		(1)
$Cd\,CO_3$	$[Cd^{2+}]$	$[CO_3^{2-}]$	$2.5 \cdot 10^{-14}$		(1)
$Fe(OH)_2$	$[Fe^{2+}]$	$[OH^{-}]^2$	$1.65 \cdot 10^{-15}$		(2)
$Mn(OH)_2$	$[Mn^{2+}]$	$[OH^{-}]^2$	$7.1 \cdot 10^{-15}$		(2)
Hg_2CO_3	$[Hg^{+}]^2$	$[CO_3^{2-}]$	$9 \cdot 10^{-17}$		(1)
Hg Cl	$[Hg^{+}]$	$[Cl^{-}]$	$2 \cdot 10^{-18}$		(1)
Zn, S, β	$[Zn^{2+}]$	$[S^{2-}]$	$1.1 \cdot 10^{-24}$		(1)
Ni S	$[Ni^{2+}]$	$[S^{2-}]$	$1 \cdot 10^{-26}$	(20°C)	(1)
$Sn(OH)_2$	$[Sn^{2+}]$	$[OH^{-}]^2$	$5 \cdot 10^{-26}$		(1)
Pb S	$[Pb^{2+}]$	$[S^{2-}]$	$3.4 \cdot 10^{-28}$	(18°C)	(1)
Sn S	$[Sn^{2+}]$	$[S^{2-}]$	$8 \cdot 10^{-29}$		(3)
$Fe(OH)_3$	$[Fe^{3+}]$	$[OH^{-}]^3$	$4 \cdot 10^{-38}$		(2)
$Sb(OH)_3$	$[Sb^{3+}]$	$[OH^{-}]^3$	$4 \cdot 10^{-42}$		(1)
Cu_2S	$[Cu^{+}]^2$	$[S^{2-}]$	$2 \cdot 10^{-47}$	(18°C)	(1)
Ag_2S	$[Ag^{+}]^2$	$[S^{2-}]$	$1 \cdot 10^{-51}$		(2)
$Sn(OH)_4$	$[Sn^{4+}]$	$[OH^{-}]^4$	$1 \cdot 10^{-56}$		(1)

may be a natural or a man-made effect. It has been studied at waste sites underlain by aquifers 8-11 m of Quaternary sands and gravels, where the groundwater is polluted to high degrees by organic and inorganic matter which are entrained into the groundwater by the seepage water or by direct contact with the waste materials (G o l w e r et al., 1970).

ADSORPTION AND ION EXCHANGE

The underground materials, both inorganic and organic, have surfaces with small unbalanced electrical charges which attract ions from the groundwater. The forces which bind these ions range from v a n d e r W a a l s forces to chemical adsorption by valence bonds. Valence bond ions are eventually adsorbed into the internal structures of the minerals. This adsorption mechanism is important for the ion exchange where equivalent quantities of bound ions are displaced by other ions from the solution. The most effective adsorbing substances in the ground are clay minerals zeolithes, hydroxides of iron and manganese, humic substances, plant roots, microbial slimes and micro-organisms.

The aquifers with the best sorptive effects and exchange capacity are permeable sediments containing small quantities of clay or humic substances. Fissured and karstified rocks have low sorption capacity.

Direction, extent and velocity of an ion exchange process depends upon the relative concentration and the properties of the involved ions and of the foreign ions. The exchange processes are reversible and can be described by the law of mass action. The intensity of the bond is different for the various ions and exchange substances. The intensity increases with the valence state and within one valence state with the atomic number and probably with the ion radius.

Selective adsorption of some ions are found: oxidhydrats of iron favour zinc, copper, lead, mercury, chromium, molybdenum, tungsten and vanadium whereas the oxidhydrats of manganese prefer copper, nickel, cobalt, chromium, molybdenum and tungsten and clay minerals zinc, copper, lead and mercury (K r a u s k o p f, 1956). Adsorption is an important factor in the prevention of widespread groundwater contaminations by heavy metals, such as an environmental lead contamination caused by traffic exhaust. Lead for the largest part is adsorbed into the humic upper part of the soil. G o l w e r (1973) studied the movement of lead near a traffic circle down to the groundwater surface, about 16 m deep. In this area the aquifer and the unsaturated zone are Quaternary sands and gravels. The lead content of the soils depends especially upon the average daily traffic (ADT) of the locality, of the age of the road and the prevailing wind direction. With growing distance from the road the concentration diminishes, especially within the first 20 meters. At the traffic circle, where in 1971 an ADT of 8200 vehicles (trucks 10-17 percent) has been measured the lead content in the uppermost layer of the soil (0-1 cm depth) 0,15 m east of the margin of the road increased since the road construction in July 1970 from probably 10-40 ppm (the average value of uncontaminated soil of this region) to 800 ppm in February 1973. The lead content of the seepage water which originally was only 0.2 ppb increased after road construction till July 1972 to 30 ppb, but decreased afterwards eventually to 3 ppb. The groundwater in this locality showed values of 3 to 9 ppb. The lead issued with the waste gases of vehicles is deposited to about 20 percent near the road and to about 80 percent is distributed in aerosols. Therefore, the lead hazard to groundwater is not restricted to the neighbourhood of roads but also affects larger regions and their groundwater recharge. The extent of this environmental damage depends upon the mobility of the lead compounds enriched in the upper layers of the ground. G o l w e r suggests that in his area of investigation the natural lead content of the upper layers of the soil is 5-10 ppm, superimposed by a regional man-made contamination of 10-30 ppm and by a local man-made contamination by roads of some 100 ppm. It is supposed that the lead reacts with sulfate- and carbonate-ions and humic or clayey complexes in the soil thus forming poorly soluble compounds and geochemical immobile agglomerates. This may be the reason of the fast diminuation of lead content with increasing depths (M a t t h e s s, 1972).

CONTAMINATION OF GROUNDWATER BY HEAVY METALS

Heavy metals are used in various ways, as raw materials for numerous industrial products or as catalysts in chemical processes. Some of them are constituents of pesticides or fertilizers which are distributed over large areas in connection with industrial, agricultural or hygienic activities. Principally all heavy metals may act as contaminants in gaseous, liquid or solid wastes. Appreciable amounts of some heavy metals are set free by the combustion of fossil fuels.

Indirect contaminations may be due to organic pollutions which produce reducing Eh-values in the groundwater thus solving iron and manganese (Kölle & Sontheimer, 1968, 1969).

Radioactive heavy metals may occur as fission-products in connection with the processing and smelting of uranium ores, the production and renovation of nuclear fuel and explosives, the disposal of nuclear contaminated cooling water and the escape of volatile radionuclides at nuclear power plants and of the various radionuclides used for medical or technical purposes. The use and disposal of radioactive material is controlled by the respective laws, which may be considered as a model for environmental protection against any dangerous element or compound.

Gaseous wastes which are apt to propagate a contamination within very short time intervals over wide areas usually contain some heavy metals in small quantities, e.g. the above mentioned lead and the fallout-radionuclide ruthenium-106 (Aurand et al., 1971, 1972).

Waste water, especially of industrial origin, contains heavy metals in higher or lower concentrations. As examples a spectacular case of groundwater contamination by galvanic waste water (Perlmutter et al., 1963) and experiences with the disposal of radioactive wastes are referred to. Cadmium and hexavalent chromium form galvanic waste waters travelled 1260 m in a Quaternary sand and gravel aquifer on Long Island since 1942. The heavy radio-nuclides in wastes containing fission-products have different mobilities in the ground (Aurand et al., 1972; Schulze & Haberer, 1966). A relatively high mobility shows ruthenium due to its chemical behaviour of forming either anionic or cationic compounds. Thus ruthenium is sometimes used as an indicator for an approaching mass of radioactive waste water (Brown & Raymond, 1962). The extension of a contaminated groundwater zone depends upon the groundwater velocity and the quality of the aquifer in relation to ion exchange and adsorption capacity, diffusion and dispersion and chemical precipitation and coprecipitation.

Solid wastes, dumps and residues of mining, ore processing and smelting operations are commonly sources of higher local concentrations of heavy metals in the groundwater (Matthess, 1972; Schöttler, 1972).

High concentrations of heavy metals in groundwater may be found in mining districts where modern leaching methods applying chemical solvents or microbial oxidation of sulfide ores are used (Nöring, 1973).

TABLE 4
Maximum permissible concentrations (MPC) of heavy metals in drinking water (in ppb)

Metal	Europe (WHO-European Standards 1970) drinking water	USA (US Publ. Health Serv. 1962) drinking water	USSR 1967 raw water
Ag	—	50	—
Cd	10	10	10
Co	–	–	1000
Cr VI	50	50	100
Cr III	–	–	500
Cu	50	(1000)*	100
Fe	100	(300)*	500
Hg	–	5 **	5
Mn	50	(50)*	–
Mo	–	–	500
Ni	–	–	100
Pb	100	50	100
Sb	–	100 **	50**
V	–	–	100
Zn	5000	5000	1000

* Maximum recommended concentrations.
** Recommended for standardization.

HEAVY METALS IN GROUNDWATER AND THEIR PHYSIOLOGICAL EFFECTS

The heavy metals may have beneficial or noxious effects on human health, partly depending on their concentration. Cobalt and zinc are trace nutrients, tin and vanadium have presumably beneficial effects, the latter preventing heart diseases. Nevertheless the incorporation of 60 mg Zn/day may give rise to acute toxic effects and some indications exist that zinc may induce cancer in mice (Haberer & Normann, 1971).

Other heavy elements are toxic, especially when they accumulate in the human body in certain organs: for instance cadmium and mercury in the liver, the kidneys and the tissues, chromium in the liver, lead in various organs. The most spectacular poisoning by heavy metals were the itai-itai disease, a shrinking of the skeleton due to a removal of calcium caused by cadmium (Yamagata & Shigematsu, in print) and the minimata disease, an irreversible damage, often fatal, of the nervous system, caused by mercury. They were essentially not due to polluted drinking water but to the metal contents of food (Gavis & Ferguson, in print). Higher amounts of chromium cause damages to the liver and kidneys, of copper damages to the liver, and of nickel damages to the nervous system. Nickel can furthermore cause dermatitis in sensitive persons. There are some suspicions that chromium has cancerogenic effects (Haberer & Normann, 1971).

Table 4 represents the maximum permissible concen-

TABLE 5
Maximum permissible concentrations MPC of radioactive heavy metals in drinking water (1. Strahlenschutzverordnung 1965).

Element	Mass number of Radio isotope	Half-Life	Radiation	MPC above natural background in solution in water (pCi/l)
Cerium	144	285 d	β^-, γ	1.10^5
Chromium	51	27,8 d	γ	2.10^7
Cobalt	57	267 d	γ	5.10^6
Plutonium	238	86,4 a	α, γ	5.10^4
	239	2.10^4a	α, γ	5.10^4
	240	6580 a	α	5.10^4
	242	$3{,}8.10^5$a	α	5.10^4
Radium	226	1620 a	α, γ	1.10^2
	228	6,7 a	β^-	3.10^2
Ruthenium	103	40 d	β^-, γ	8.10^5
	106	385 d	β^-, γ	1.10^5
Uranium	235	$7{,}1.10^8$a	α, γ	3.10^5
	238	$4{,}5.10^9$a	α, γ	4.10^5
Zinc	65	245 d	β^-, γ	1.10^6

trations of several heavy metals. The limits of antimony, cadmium, chromium, lead and mercury are based on their adverse physiological effect. The limits of such substances as iron, manganese, copper and molybdenum are much lower than the concentrations impairing the health, but are established to prevent objectionable taste, color, turbidity or stains.

The MPC for radioactive heavy elements (table 5) takes into consideration their different physiological behaviour in human body. Some of them tend to accumulate in certain parts of the body thus concentrating their dangerous radiation to restricted areas. For example plutonium and radium will accumulate in the bones. On the other hand the MPC of uranium 238 (4.10 pCi/l) which is equivalent to about 120 ppm uranium is not exceeded in natural water. But the danger from its chemical toxicity which causes liver damage is greater than the danger from radiation. (D a v i s & d e W i e s t, 1967; A r n d t et al., 1973).

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