

## **Presence and significance of naturally occurring chemical elements of the periodic system in the plant organism and consequences for future investigations on inorganic environmental chemistry in ecosystems**

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### **Abstract**

After acceptance of the 'Element Concentration Cadasters in Ecosystems' (ECCE) programme as an international project sponsored by the International Union of Biological Sciences (IUBS) at the 24th General Assembly of IUBS in Amsterdam in Sept 1991, the present status of 'Biological Trace Element Research' (BTER) is presented here from the biological point of view. Especially information on occurrence, essentially, toxicity and uptake form of all 88 naturally occurring chemical elements is presented. In addition an estimated annual production of each element in the year 2000 and examples of their technical application is given. A scientific proposal for further research work on a local, regional and global scale has been discussed.

The earth's crust may be regarded as a natural reservoir for all the chemical elements of the biosphere. More than 99% of the total mass of the earth's crust is formed from only 8 of the 88 naturally occurring elements. It consists of 46.4% oxygen, 28.15% silicon, 8.23% aluminium, 5.63% iron, 4.15% calcium, 2.36% sodium, 2.33% magnesium and 2.09% potassium (Bowen 1979; Fiedler & Rösler 1988; Kovalskij 1977). Oxygen is the only non-metal among the 8 most frequent elements in the earth's crust. The remaining 80 elements of the periodic table represent less than 1% of the composition.

The major fraction of the fresh weight of living plant organs, i.e. those displaying an active metabolism, consists on average of 85–90% water. The dry substance of the plant body is mainly

composed of the following elements: carbon (44.5%), oxygen (42.5%), hydrogen (6.5%), nitrogen (2.5%), phosphorus (0.2%), sulphur (0.3%) and the alkali and alkaline-earth metals potassium (1.9%), calcium (1.0%) and magnesium (0.2%) (Bazilevich & Rodin 1966; Clüsener Godt 1990; Duvigneaud & Denaeyer de Smet 1968a and b, 1973; Fortescue 1980; Heinrichs & Mayer 1980; Newbould 1967; Rodin & Bazilevich 1967). In contrast to the earth's crust, the main mass of organic life is therefore predominantly formed of non-metals (Fig. 1). On the basis of their increased occurrence in the plant vegetation body the nine elements mentioned above are also termed macroelements. In addition, there are also so-called microelements occurring in the plant organism in lower concentrations and vital for most

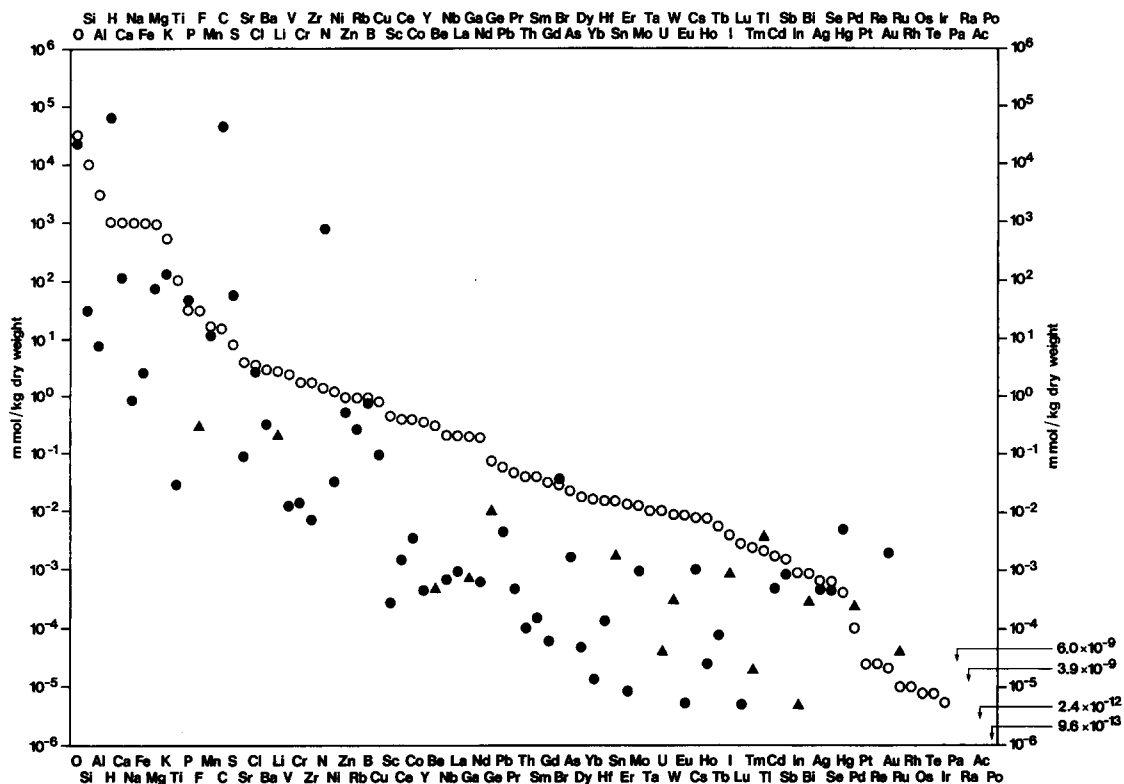


Fig. 1. Concentration of 82 naturally occurring elements (with the exception of the inert gases) in plants and the earth's crust (from Markert 1991b). The elements are plotted according to decreasing occurrence in the earth's crust. ●: concentration in the earth's crust (from Bowen 1979); ○: concentration in plants after Markert 1986; ▲: concentration in plant material after Bowen 1979.

plants. These elements are chlorine (2000 mg/kg dry substance), silicon (1000 mg/kg), manganese (200 mg/kg), sodium (150 mg/kg), iron (150 mg/kg), zinc (50 mg/kg), boron (40 mg/kg), copper (10 mg/kg), chromium (1.5 mg/kg), molybdenum (0.5 mg/kg) and cobalt (0.2 mg/kg).

Both macro- and also microelements are plant nutrients vital for the growth and normal development of the plant and their function cannot be replaced by any other element. They are thus essential (Fig. 2). Macro- and microelements are therefore also known as macro- and micronutrients. However, it does not always seem appropriate to divide the periodic system into essential and non-essential elements since there are numerous exceptions within the plant kingdom, which are particularly striking in a comparison of higher and lower plants. In some bacteria and fungi, for example, calcium, boron and chlorine, or in higher

plants sodium and silicon are not regarded as essential (Marschner 1983).

Apart from the macro- and micronutrients discussed above, a number of further chemical elements also occur in plants (Adriano 1986; Bodeck *et al.* 1988; Hamilton 1979 and 1980; Caroli *et al.* 1990). Fig. 3 shows those elements which were quantitatively detected in a time-consuming analytical cycle (Markert 1986). In this Figure it is conspicuous that the elements lanthanum, cerium, barium, bromine and many others occur in mass concentrations similar to the micronutrients discussed above. The increased utilization of instrumental multielement techniques for biological investigations will probably ensure that the essential character of further elements will be recognized in future (Ernst 1990; Golley 1978; Likens 1977; Roth-Holzappel 1990; Sansoni 1985; Vanoeteren *et al.* 1986; Markert & Thornton 1990; Markert

H																			He
Li?	Be											B	C	N	O	F	Ne		
Na	Mg											Al	Si	P	S	Cl	Ar		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
Rb	Sr	Y	Zr	Nb	Mo	Tc*	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po*	At*	Rn*		
Fr*	Ra*	Ac*																	

Ce	Pr	Nd	Pm*	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th*	Pa*	U*	Np*	Pu*	Am*	Cm*	Bk*	Cf*	Es*	Fm*	Md*	No*	Lr*





 : essential for plants and animals      ? : essentiality will be discussed  
 : essential for plants only       : in addition quantitatively determined in plants within an interlaboratory comparison  
 : essential for animals only      • : all nuclides of this element are radioactive

Fig. 2. The periodic system of elements with data on essential and quantitatively detected elements (from Markert 1991b).

& Zhang de Li 1991; Markert 1992a). The elements fluorine, iodine, nickel, selenium, tin and vanadium are already regarded as essential for animal organisms. Further elements are under discussion including some which until recently were only considered from a toxicological point of view (e.g. cadmium and lead). There are currently indications that in a correspondingly low concentration these elements exercise metabolic functions in living organisms (Anke 1989a and b; Brätter & Schramel 1988; Hemphill, 1967–1989). In general it may be assumed, as already postulated by Horovitz in 1988 due to the ubiquity of all chemical elements, that all elements also have a physiological significance and that a separation into essential and non-essential elements does not exist in nature. The fact that elements to which little attention has been paid as yet are in fact essential can only be determined by correspondingly extensive efforts in further analytical chem-

ical multielement investigations where an integrated approach is an absolute necessity taking into consideration all chemical elements.

In the same way as the division into essential and non-essential elements, the classical division into micro- and macroelements discussed above, which solely refers to the physical mass of an element within the organism, has received essential modifications in modern plant, animal and human physiology. The list of macroelements has had to be extended for certain groups of organisms. Thus for example, the element silicon is regarded as a macroelement for Sphenopsida and diatoms. Furthermore, due to specific site conditions, element- or organism-specific accumulation processes frequently occur: sodium, bromine and chlorine are accumulated by many halophytes (Markert & Jayasekera 1987); copper, nickel, zinc, lead, cadmium and other heavy metals are taken up by metallophytes to an increased extent

ECC of	<i>Vaccinium vitis-idaea</i> (leaves) (red whortleberry)										Osnabrück Achmer	E: 7° 50' N: 52° 20' 68 NN	8,8° C 771 mm	rainy	
17.6.1983	on Podsol											AAS AES-ICP MAS NAA, EA	D: 48h/105° C W: – H: agate/10 min	De: conc. HNO <sub>3</sub> 3h, 170° C 2-4 Torr	
10 <sup>2</sup> mg/kg	-6	-5	-4	-3	-2	-1	0	1	2	3	4	5	6	detection limit	not determined
				Eu	Lu	Gd	Sb	Tl	B	Fe	P	N	O	Bi < 0.1	Ac, Ar, At,
					Er	Tb	As	Br	Nd	Cl	Mg	H	C	Ga < 0.02	Be, <span style="border: 1px solid black; padding: 0 2px;">B</span> ,
					Yb	Sc	La	Ni	Rb	Al	S			Ge < 1	Fr, He, <span style="border: 1px solid black; padding: 0 2px;">I</span> ,
					Au	Hg	Cg	Cu	Zn	Mn	Ca			Sn < 0.2	In, Ir, Kr,
					Ho	Hf	Ce	Sr	Ba	Si	K			Tm < 0.1	Li, Ne, Os,
					Dy	Sm	Zr							U < 0.073	Pa, Pd, Pm,
						Th	Cs							W < 0.057	Po, Pt, Ra,
						Y	V								Re, Rh, Rn,
						Se	Pb								Ru, Ta, Tc,
						Ag	Cr								Te, Ti, Xe
						Cd									
						Nb									
						Pr									
						Nd									
						Md									

Fig. 3. Element concentration cadaster for *Vaccinium vitis-idaea* (red whortleberry, leaves); —: middle of the concentration class; D: drying conditions; W: washing conditions; H: homogenization conditions; De: ashing or decomposition conditions; ○: only essential for plants; □: essential for plants and animals; ■: only essential for animals (modified after Lieth & Markert 1990).

(Ernst 1974; Ernst & Joosse Van Damme 1983). The essentiality, occurrence, toxicity and uptake form of individual elements in the environment is given in Appendix 1. The estimated annual production of single elements for the year 2000 and examples of their technical application is given in Appendix 2. A rough estimation of the total element content in the world plant biomass is given in Table 1.

Admittedly, an accumulation is not to be equated with an increased physiological benefit from the element for the organism, indeed this probably often purely represents an adaptation to the respective site (Kovacs 1982; Kovacs *et al.* 1990; Kinzl 1982; Markert & Weckert 1989; Markert & Klausmeyer 1990; Wiersma *et al.* 1987; Mengel 1984; Markert 1988). Nevertheless, the above examples help to show difficulties involved in a systematic classification of chemical elements on the basis of their physical mass. It may frequently be observed that a macro- and a micronutrient behave physiologically in a much

more similar manner than two micro- or macro-nutrients (Mengel 1984). Since the significance of an element for the plant does not depend on its volume fraction in the plant substance, a systematic division according to physiological and biochemical aspects, as attempted in Table 2 on the basis of Sansoni and Iyengar (1978), seems more meaningful. The elements described as structural elements are those involved in the constitution of functional molecular units of the cell metabolism (proteins, lipids, carbohydrates, nucleic acids) or display a direct supporting or strengthening character (calcium, silicon). Nitrogen and sulphur are biochemically integrated into the carbon chain, i.e. stably bound to the organic substance after reduction of their generally high oxidation stage (nitrate or sulphate). In contrast, phosphorus, boron and silicon are present in their highest oxidation stage and are not reduced, but rather tend towards ester formation with OH groups of the most varied molecules, particularly the sugars (Mengel 1984). On the other hand, the so-called

Table 1. Estimation of the total element content in the world plant biomass in *t*.

Ac	?	Hf	$9,2 \times 10^4$	Rb	$9,2 \times 10^7$
Ag	$3,682 \times 10^5$	Hg	$1,841 \times 10^5$	Re	?
Al	$1,47 \times 10^8$	Ho	$1,472 \times 10^4$	Rh	$1,84 \times 10^1$
As	$1,841 \times 10^5$	I	$5,523 \times 10^6$	Ru	$1,84 \times 10^1$
Au	$1,841 \times 10^3$	In	$1,841 \times 10^3$	S	$5,523 \times 10^{10}$
B	$7,3640 \times 10^7$	Ir	$1,841 \times 10^2$	Sb	$1,841 \times 10^5$
Ba	$7,3640 \times 10^7$	K	$3,497 \times 10^{10}$	Sc	$3,682 \times 10^4$
Be	$1,841 \times 10^3$	La	$3,682 \times 10^5$	Se	$3,682 \times 10^4$
Bi	$1,841 \times 10^4$	Li	$3,682 \times 10^5$	Si	$1,841 \times 10^9$
Br	$7,364 \times 10^6$	Lu	$5,523 \times 10^3$	Sm	$7,364 \times 10^4$
C	$8,19 \times 10^{11}$	Mg	$3,682 \times 10^5$	Sn	$3,682 \times 10^5$
Ca	$1,841 \times 10^{10}$	Mn	$3,682 \times 10^8$	Sr	$9,2 \times 10^7$
Cd	$9,2 \times 10^4$	Mo	$9,2 \times 10^5$	Ta	$1,841 \times 10^3$
Ce	$9,2 \times 10^5$	N	$4,602 \times 10^{10}$	Tb	$1,472 \times 10^4$
Cl	$3,682 \times 10^9$	Na	$2,76 \times 10^8$	Te	$9,2 \times 10^4$
Co	$3,682 \times 10^5$	Nb	$9,2 \times 10^4$	Th	$9,2 \times 10^3$
Cr	$2,7615 \times 10^6$	Nd	$3,682 \times 10^5$	Tl	$9,2 \times 10^4$
Cs	$3,682 \times 10^5$	Ni	$2,76 \times 10^6$	Ti	$9,2 \times 10^6$
Cu	$1,841 \times 10^7$	O	$7,824 \times 10^{11}$	Tm	$7,364 \times 10^3$
Dy	$5,523 \times 10^4$	Os	$2,7615 \times 10^1$	U	$1,841 \times 10^4$
Er	$3,682 \times 10^4$	P	$3,682 \times 10^{10}$	V	$9,2 \times 10^3$
Eu	$1,472 \times 10^4$	Pa	?	W	$3,682 \times 10^5$
F	$3,682 \times 10^6$	Pb	$1,841 \times 10^6$	Y	$3,682 \times 10^5$
Fe	$2,76 \times 10^8$	Pd	$1,841 \times 10^2$	Yb	$3,682 \times 10^4$
Ga	$1,841 \times 10^5$	Po	?	Zn	$9,2 \times 10^7$
Gd	$7,364 \times 10^4$	Pr	$9,2 \times 10^4$	Zr	$1,841 \times 10^5$
Ge	$1,841 \times 10^4$	Pt	$9,2 \times 10^1$		
H	$1,196 \times 10^{11}$	Ra	?		

electrolytic elements are required for the construction of specific physiological potentials and are important for maintaining defined osmolytic conditions in the cell metabolism. The element calcium may thus appear simultaneously as a structural element and an electrolytic element. A number of chemical elements, above all metallic ions, exercise a catalytic function in the cell metabolism as a metal complex compound (Irgolic & Martell 1985). These elements are termed enzymatic elements in Table 2. The physiology of these elements in the metabolism is described in detail in textbooks on plant, animal and human biology.

The relationship between the nutrient supply in the substrate (soil, nutrient solution, atmosphere) and activity of the plant is in a wide range not linear but rather describes an optimum curve which may display either a symmetric (Fig. 4a, c, d) or asymmetric course (Fig. 4b, e), close

(Fig. 4b, d, e) or wide (Fig. 4a, c) tolerance limits. The curve of this type of dose-effect relation depends on the plant species in question, the element species and the respective site conditions. In general, the activity is equal to zero if an essential nutrient element is completely lacking; the organism is not viable. Whether individual elements are essential for photoautotrophic plants has generally been determined to date by cultivation on defined composition media as nutrient solutions (Baumeister & Ernst 1978; Brümmer 1986; Epstein 1972; Fränzle 1990). In recent years it has become apparent that it is difficult to determine experimentally in the trace range, and quite particularly in the ultratrace range, whether an element actually has no influence on the growth of a plant organism since very often even minute quantities of the element are sufficient to prevent deficiency symptoms in the organism (Kiem & Feinendegen 1985; Iyengar *et al.* 1988; Mertz

Table 2. Division of the chemical elements according to physiological aspects.

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Structural elements:	C, H, O, N, P, S, Si, Ca
Electrolytic elements:	K, Na, Ca, Cl, Mg
Enzymatic elements:	V*, Cr, Mo, Mn, Fe, Co, Ni*, Cu, Zn, B**, Sn*, Se*, F*, I*, Mg

Up to now without biological function:

1 <sup>st</sup> main group: Li, Rb, Cs, (Fr)	2 <sup>nd</sup> main group: Be, Sr, Ba, Ra
3 <sup>rd</sup> main group: Al, Ga, In, Tl	4 <sup>th</sup> main group: Ge, Pb
5 <sup>th</sup> main group: As, Sb, Bi	6 <sup>th</sup> main group: Te, Po
7 <sup>th</sup> main group: Br, (At)	
8 <sup>th</sup> main group: He, Ne, Ar, Kr, Xe, Rn	
1 <sup>st</sup> subgroup: Sc, Y	2 <sup>nd</sup> subgroup: Ti, Zr, Hf
3 <sup>rd</sup> subgroup: Tb, Ta	4 <sup>th</sup> subgroup: W
5 <sup>th</sup> subgroup: (Tc), Re	6 <sup>th</sup> subgroup: Ru, Os
7 <sup>th</sup> subgroup: Rh, Ir	8 <sup>th</sup> subgroup: Pd, Pt
9 <sup>th</sup> subgroup: aG, Au	10 <sup>th</sup> subgroup: Cd, Hg

Lanthanides: La, Ce, Pr, Nd, (Pm), Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu.

Actinides: Ac, Th, Pa, U, (Np), (Pu), (Am), (Cm), (Bk), (Cf), (Es), (Fm), (Md), (No), (Lr).

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( ): Elements not naturally occurring based on Sansoni and Iyengar (1978).

\*: Essential significance only determined for animal organisms as yet.

\*\* : Essential significance only determined for plant organisms as yet.

1981 and 1986–1987). Sufficient quantities may be present as impurities in the nutrient substrate, in the external air or the container material, frequently in such slight quantities that the elements are difficult to determine by analytical methods.

To this end, experimental plants are kept in an environment intended to largely prevent a contamination by trace elements. Insulators made of various plastics are used today because they do not release the trace elements contained in them as readily as glass or metals for example (Loeffler *et al.* 1979). The trace elements contained in the atmospheric dust are removed by powerful air filters. The plants receive nutrition consisting of chemically pure amino acids (instead of proteins which often contain microelements in a stable bond) and other substances; the trace element regarded as essential is not included. If this element is vital then observable or measurable metabolic disturbances occur which can usually be eliminated by supplying normal food. In the same

way as the contamination difficulties arising during work in the ultratrace range at every analytical chemical laboratory, it cannot be ruled out in these experiments that the lack of any physiological metabolic disturbance only simulates 'non-essentiality' because the element in question is already present in sufficient concentrations in the form of impurities in the substrate or laboratory air.

Insufficient supply of an element from the nutrient medium frequently leads to the appearance of deficiency symptoms. These symptoms can be prevented by adding a slight (Fig. 4a, b) or larger (Fig. 4c, d, e) quantity of nutrient substance. The activity of the organism reaches its maximum with an adequate nutrient supply. An increased nutrient supply does not lead to an increase in activity at first. This remains constant over a wide (Fig. 4a) or narrow (Fig. 4b, c, d, e) range of substrate concentration (nutrient saturation). A further substrate supply first leads to toxicity symp-

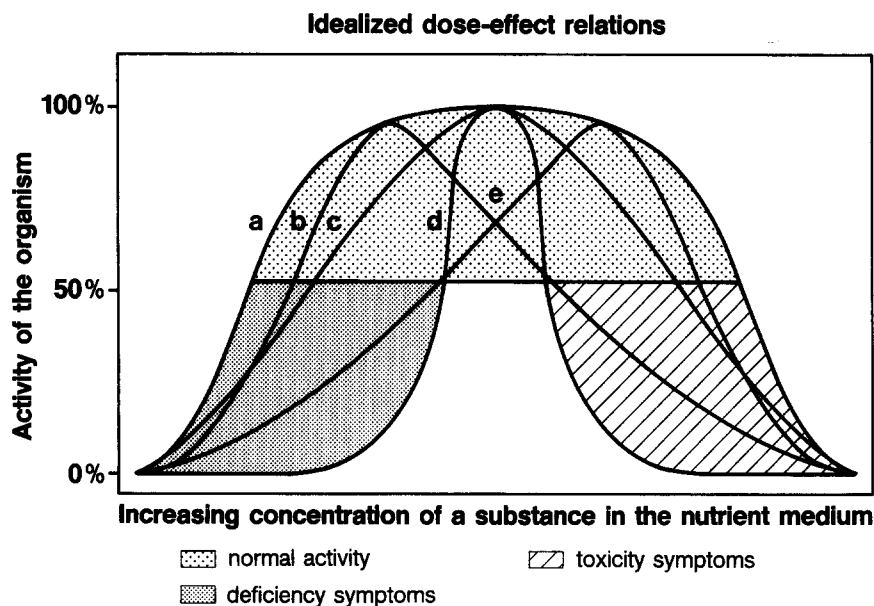


Fig. 4. Idealized dose-effect relations between substrate concentration and activity of the organism (from Markert 1992a).

toms and finally to the organism's death. In this case the statement formulated by Paracelsus nearly 500 years ago remains true of all chemical substances whether toxic, essential or indifferent:

'Is there anything that isn't poisonous? Everything is poisonous – only the dose determines whether something is poisonous or not.'

The unambiguous description of the effect of a certain element is frequently made more difficult by the presence of other substances frequently with a similar ionic radius and the same charge since it is not usually the concentration of one individual element or individual element species which is responsible for the healthy growth and normal development of an organism but rather a balanced ratio between the individual elements or element species. Interelemental interactions in the sense of competitive inhibition or promotion may be of decisive influence for the physiology of individual organisms.

Quantitatively, the ingestion is adequately described by the intensity and extent of uptake up to a certain point in time. With a defined nutrient, the uptake by the plant depends on the reserves of the nutrient in the uptake medium and its availability (Iserman 1979). As a rule, the plant does

not have a positive influence on the reserves, but rather on the material and spatial availability of the nutrients. Thus, for example, the nutrient availability may be altered from the material aspect by influencing the pH value of the soil solution (excretion of  $\text{H}_3\text{O}^+$  or  $\text{HCO}_3^-$  ions through the root), by releasing chelating organic acids from the root or else assisted by microorganisms (mycorrhiza) as well as by an influence on the redox potential in the soil by  $\text{H}_3\text{O}^+$  and  $\text{O}_2$  deposition at the root surface (Iserman 1979). The most readily available elements are present in the form of ions or a soluble organic complex in the soil solution. The elements with the poorest availability are stably bound to the soil structure, e.g. in the form of minor constituents in the crystal structure of primary minerals. The most important source between these extremes is small particles with a large surface loaded with metals, e.g. clay, sludge and organic material. Altogether, this may be termed the 'exchange complex' (Berrow & Burridge 1984). Ions may be exchanged for each other at the surfaces, for example calcium for magnesium, potassium or hydrogen.

The intensity and extent of the uptake therefore influence the actual content of an element in the

plant organism. Three uptake types may be roughly differentiated as a function of the plant species under consideration, the element species and the specific site conditions (Fig. 5). In the ideal case, there is a direct proportionality between the nutrient supply and uptake by the plant organism. In this case, the specific element content of the plant reflects the concentration relations in the nutrient substrate. The chemical plant composition thus has an indicative character. This relationship, which has been observed for a number of plants and various elements both experimentally and also in the field, is being increasingly applied in practice, e.g. in ore prospecting or the use of (usually lower) plants for environmental monitoring (biomonitoring). Due to unfavourable site conditions, many plants have developed the property of accumulating high concentrations of individual elements, frequently irrespective of whether these elements have a physiological benefit or not. These plants are termed accumulators. Thus for example, some Ericaceae are distinguished by a high element content of manganese, irrespective of the content in the soil, and birch by a high zinc content. This accumulative behaviour, which is not site-conditioned but may possibly be due to genetically predetermined causes, enables chemical fingerprinting to be carried out with the

most varied plant species. In future this may lead to a chemical characterization and thus to a systemization of individual plant species which on a phytosociological level may provide information about evolutionary processes. Less frequently than element accumulation, but nevertheless already determined for numerous plant species, rejection may occur, i.e. a reduced uptake of individual elements. The reduction in the concentration of an element in the organism may result from a complete or partial exclusion. According to Ernst and Joosse Van Damme (1983), bacteria, algae and higher plants have heavy-metal-resistant populations which are capable of considerably reducing the uptake of heavy metals by excreting mucilaginous substances or by altering the cell walls.

The above discussion reveals the difficulties and also the enormous possibilities associated with increased multielement research, particularly with environmental specimens.

In an ecosystem the paths and persistence of the elements may be specifically influenced by organismic activities, e.g. by a selective element uptake and concentration. Elements occurring together may therefore influence their transport or accumulation within the organism positively and/or negatively (Adriano 1986; Kabata-Pen-

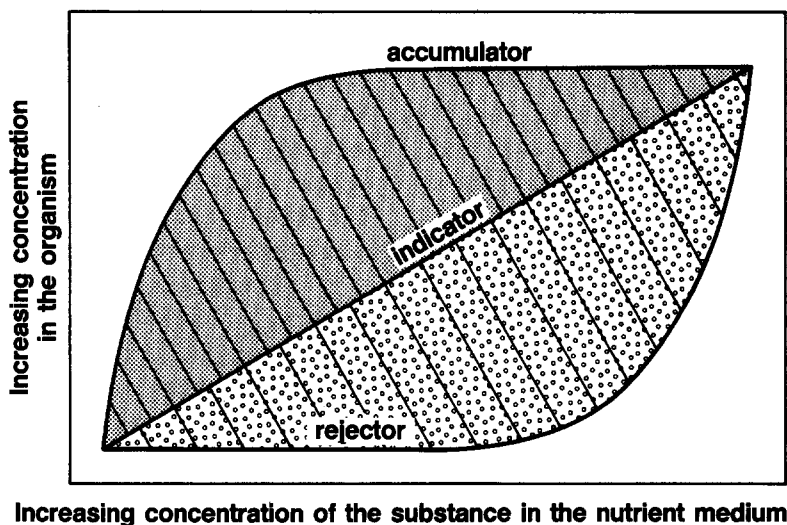


Fig. 5. Different uptake behaviour of living organisms with respect to substrate concentration (from Markert 1991c).



dias & Pendias 1984; Marschner 1983 and 1986; Lieth *et al.* 1989). Antagonistic element behaviour might be explained by competition for the same bonding location in the organism.

Many plants are in a position to take up large quantities of certain elements from the environment. It has thus been possible to demonstrate that birch trees accumulate zinc, Ericaceae manganese and individual species of moss specific heavy metals. At the same time, the need is covered for other trace elements for the growth of these plants. It is possible that the metabolic significance of several elements has not yet been recognized so that the division frequently encountered in the literature into essential and non-essential elements requires continuous revision (Horovitz 1988; Markert 1991a and b). Biological trace element research is thus a dynamic process and a number of new insights are to be expected in future (Freedman 1989; Irgolic & Martell 1985; Iyengar 1988 and 1989; Markert 1992c; McKenzie & Smythe 1988; Nriagu & Pacyna 1988; Schramel & Li-Qiang Xu 1991; Tölg 1989; Zeisler *et al.* 1988).

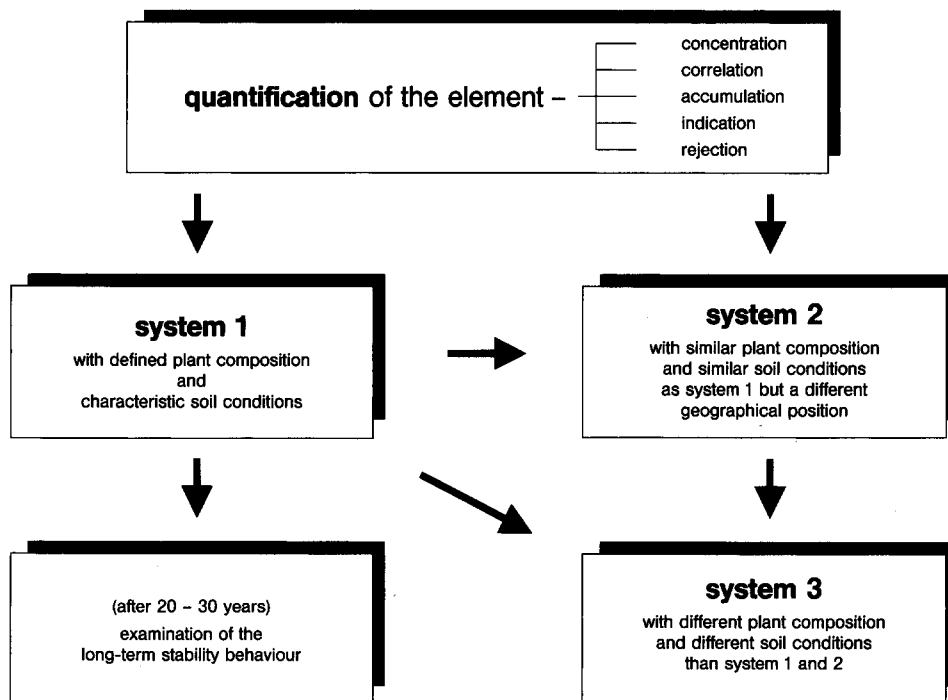
It may be assumed that interrelations between organismic activity and flow rates, as well as flow patterns of the elements, arise from the various components and compartments of an ecosystem which can only be correctly interpreted with analytical coverage of, if possible, all elements (Jayasekera 1987; Lieth & Markert 1985; Markert & Wtorowa 1992). Undoubtedly, the nature and extent of this reciprocal influence is for most elements and ecosystems dependent on abiotic factors such as weather factors. Consequently the flow rates and flow patterns vary as a function of these factors. This must always be remembered when interpreting ecochemical data. The results are only characteristic of the factor constellation prevailing during sample collection (Lieth & Markert 1988a and b, 1990; Markert 1992c). The preliminary history of the sample material should also be included in a description of the factor constellation (Markert & Wtorowa 1992).

Depending on the components of an ecosystem to be investigated, how often sampling took place and the possibility of making comparisons with

other ecosystems of the same type, the following interpretation possibilities arise for the data material (Markert & Wtorowa 1992 and Table 3).

- a. If the components and compartments studied in the system are immediately consecutive stages of the material flow then statements can be made on the basis of a multielement analysis concerning
  - the concentrations in which individual elements occur,
  - whether and to what extent individual elements occur in a correlated manner in the samples studied above,
  - whether the samples studied display an accumulative, indicative or rejective behaviour for certain elements.
- b. If a multielement analysis is carried out for a certain factor constellation with several ecosystems of the same type (similar soil conditions and plant composition) subjected to a different input of elements then a comparison of the data will provide initial insights into how differently comparable ecosystems may react to various material inputs. Not only simple changes in concentration ratios have to be considered here but also changes in the accumulative behaviour of individual plant species, shifts in element correlations etc.. Traditionally particular interest is attached to a consideration of those elements whose ecotoxicological significance is known.
- c. The results of multielement analyses for a factor constellation recognized as typical of an ecosystem are able, if compared with systems displaying different plant composition and soil conditions, to form a reliable basis (possibly together with other data) for a consideration and causal analysis. This provides indications of
  - whether, to what extent and under what conditions the element correlations in the individual matrices change,
  - whether, to what extent and under what conditions changes in accumulative behaviour are to be directly attributed to different soil conditions or plant-specific element patterns,

Table 3. Comparable aspects of instrumental multielement analysis in ecosystems. Comparability of single system data will be reached by harmonizing the sampling procedure, sample preparation, instrumental measurements as well as data evaluation (Markert 1992a and Markert & Wtorowa 1992).



– the factor constellations under which and to what extent concentration changes may be observed.

- d. If the results of multielement analyses are compared over a lengthy period of time for similar ecosystems only differing with respect to the material input into that system then conclusions about the stability behaviour of the system may possibly result from the aspect of the material flow (see e.g. the Environmental Specimen Banking Project described in Bundesministerium für Forschung und Technologie 1988 and Stoepler *et al.* 1982).

The experimental plan sketched above and reproduced in Table 3 shows that ecosystem multielement analyses should not be equated with the simple measurement of element concentrations. The validity or interpretability of concentration data within a series of measurements should always be regarded in view of the question in hand and the special parameter constellation. From the

biological point of view attention was focused on the concepts of concentration, correlation, accumulation, rejection and indication of individual elements or groups of elements, and from the analytical aspect specific problems concerning appropriate sampling, sample preparation and the detection sensitivity of individual instrumental methods. The goals of the studies described here may be formulated as follows (Markert & Wtorowa 1992):

a: Biological goals

- compilation of a so-called element concentration cadaster for the main plant species of a forest ecosystem in the sense of ‘fingerprinting’ (concentration aspect),
- creation of a data base for a natural ecosystem and establishing ‘natural’ basic concentrations preferably for elements rarely studied to date (concentration aspect),
- discovery of interelement relations and other regularities in the plant organism (correlation aspect),

- determination of the selection sensitivity of various plant species for individual elements or groups of elements from the periodic system and discovery of any possible accumulator properties (accumulation or rejection aspect),
  - application of plant systems for long-term pollutant monitoring in ecosystems (indication aspect).
- b. Analytical goals
- improvement of representative sampling
  - and development of a sampling programme for plant specimens,
  - optimization of sample preparation techniques (in particular washing, homogenization, drying, decomposition and ashing),
  - application and comparison of various multielement procedures for the chemical characterization of plant samples with respect to reproducibility, accuracy and concentration dependence of the analytical data.
  - speciation analysis

## Appendix 1

Essentiality, occurrence, toxicity and uptake form of individual naturally occurring elements in the environment. The uptake of many metals in the form of chelate complexes was not taken into consideration. The data were taken from different textbooks: Anke 1989a and b; Bowen 1979; Kabata Pendias & Pendias 1984; Markert 1986 and 1992a; Merian 1991; Streit 1991

Legend:

Bac: essentiality for bacteria

Alg.: essentiality for algae

Fun.: essentiality for fungi

HPl: essentiality for higher plants

An: essentiality for animals

+ : essential

- : as yet no essential significance

+ / - : essentiality only demonstrated for certain species

? : essentiality under discussion, if? refers to essentiality

S: average contents in soils (in mg/kg DW)

P: average contents in plants (in mg/kg DW)

R: average content in the reference plant (in mg/kg DW, after Markert, 1992c)

Pl: average toxicity concentration for plants

M: average toxicity concentration for man

Rat: average toxicity concentration for rats

l: lethal dose

d: daily intake

F: examples of the element function

A: accumulator organisms

De: deficiency symptoms in case of insufficient supply of the element

Sp: special features of the element

? : no information available, if? does not refer to topic essentiality

	Essentiality					Occurrence (mg/kg DW)	Toxicity	Uptake in the form of
Ac	Bac	Alg	Fun	Hpl	An	S: ? P: ? R: ?	Toxic	
	-	-	-	-	-			
	A: 15–1000 Bg/kg in plants grown on thorium-rich soils (Bowen, 1979)							
Ag	Bac	Alg	Fun	HPl	An	S: 0.02–0.09 P: 0.06–0.3 R: 0.2	Toxic M: 60 mg/d	Ag <sup>+</sup> AgCl <sub>2</sub> <sup>-</sup>
	-	-	-	-	-			
	A: Lycoperdales, Eriogonum ovalifolium							
	Sp: Used medically as an antibacterial ointment for burns (especially for <i>Pseudomonas acraginosa</i> ) and in dental fillings.							
	Interaction with Cu and Se in the metabolism							

## Appendix I. Continued.

	Essentiality					Occurrence (mg/kg DW)	Toxicity	Uptake in the form of
Al	Bac -	Alg -	Fun -	HPl -	An -	S: 71000 P: 90-530 R: 80	Toxic* Pl: 0.1-30 mg/l	Al <sup>3+</sup> Al(OH) <sub>4</sub> <sup>-</sup> Al(OH) <sub>3</sub>
A: Diapensiaceae, Ericaceae, Melastomaceae, Symplocaceae, Theaceae, Orites excelsa F: Essentiality discussed for ferns, possibly activation of some dehydrogenases and dehydrogenase enzymes Sp: *Aluminium is toxic for plants and fish. Possibly a component factor in novel forest damage since Al is made more readily available by acid deposition. Possible connection with Alzheimer's disease								
As	Bac -	Alg -	Fun -	HPl -	An* ?	S: 0.1-20 P: 0.01-1.5 R: 0.1	Toxic** Pl: 0.02-7.5 mg/l M: 5-50 mg/d	HAsO <sub>4</sub> <sup>2-</sup> H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup>
F: As is essential for red algae. De: *As deficiency causes a reduction in growth and affects reproduction in vertebrates. As deficiency leads to cardiac death in the third generation for goats. Sp: **Toxicity increases from As via As(V) to As(III)								
Au	Bac -	Alg -	Fun -	HPl -	An -	S: 0.001-0.002 P: 0.01-0.04 R: 0.001	Slightly toxic*	Au(OH) <sub>3</sub> AuCl <sub>2</sub> <sup>-</sup>
A: Possibly Tectona grandis Sp: Au is administered in organic compounds as a medicinal treatment for arthritis. *Au(III) is more toxic than Au(I)								
B	Bac ?	Alg +	Fun -	HPl +	An -	S: 5-80 P: 30-75 R: 40	Pl: 1-5 mg/l M: 4g/d	B(OH) <sub>3</sub> B(OH) <sub>4</sub> <sup>-</sup>
A: Cruciferaeae and Leguminosae F: B is of significance for cell division, possibly also involved in the glycometabolism and sugar transport, participation in flavonoid and nucleic acid synthesis, participation in cell wall construction, stimulates N-fixation by bacteria. De: Deficiency symptoms are known worldwide (disturbance in growth, restricted root branching, phloem necrosis, fructification disturbances) Sp: Borates serve for water softening in detergents which involves dangers for groundwater and irrigation water								
Ba	Bac -	Alg -	Fun -	HPl -	An -	S: 500 P: 10-100 R: 40	Rel. Harmless Pl: 500 mg/l M: 200 mg/T	Ba <sup>2+</sup>
A: Bertholletia excelsa, plankton: Chaetoceros curvisetus and Rhizosolenia calcar-avis Sp: A possible essentiality discussed for mammals								
Be	Bac -	Alg -	Fun -	HPl -	An -	S: 0.1-5 P: 0.001-0.4 R: 0.001	Toxic* Pl: 0.5 mg/l	BeOH <sup>+</sup>
A: Vaccinium myrtillus and Vicia sylvatica Sp: *Both Be metals and Be compounds are considered to be allergenic. The carcinogenicity of Be has been demonstrated for several animal species								
Bi	Bac -	Alg -	Fun -	HPl -	An -	S: 0.2 P: 60 ppb R: 0.01	Hardly toxic Pl: 27 mg/l Rat: 160 mg/d, l	BiO <sup>+</sup> Bi(OH) <sub>2</sub> <sup>+</sup>

## Appendix 1. Continued.

	Essentiality					Occurrence (mg/kg DW)	Toxicity	Uptake in the form of
Br	Bac -	Alg +/-	Fun -	HPI -	An ?	S: 1-10 M: 15 R: 4	P: 15-600 mg/l M: 3g/d	Br <sup>-</sup> BrO <sup>-</sup> HBrO
<p>A: Some red and brown algae, some Porifera, many corals, a few molluscs (Aplysia and Muricidae), fungus Amanita ssp.  F: Essentiality for mammals under discussion  Sp: Sources of bromide emissions are antiknock agents, fumigants for preservation purposes, insecticides and flame-proofing agents</p>								
C	Bac +	Alg +	Fun +	HPI +	An +	S: variable* P: 45% R: 44.5%	Many toxic compounds in the form of CO <sub>2</sub> **	CO <sub>2</sub> HCO <sub>3</sub> <sup>-</sup>
<p>F: Basic structural element of all organic compounds (sugar, fats, proteins etc.)  Sp: *Very variable, depending on soil type and soil horizon. **CO<sub>2</sub> and CH<sub>4</sub> cause the greenhouse effect, the average CO<sub>2</sub> content of the atmosphere is 340 ppm</p>								
Ca	Bac +	Alg +	Fun -	HPI +	An +	S: 0.1-1.2% P: 1% R: 1%	Hardly toxic	Ca <sup>2+</sup> CaOH <sup>+</sup>
<p>A: Some red algae, shells of many invertebrates, bone  F: Structural constituent of cell walls, constituent of bone, physiological regulation function, enzyme activator, electro-chemical function  De: Deficiency in plants causes disturbed division growth (small cells), drying of leaf tips, leaf deformation, restricted root growth</p>								
Cd	Bac -	Alg -	Fun -	HPI -	An ?	S: 0.01-3 P: 0.03-0.5 R: 0.05	Toxic** Pl: 0.2-9 mg/l M: 3-330 mg/d	Cd <sup>2+</sup> CdOH <sup>+</sup>
<p>A: Agaricus and other fungi, molluscs Ostrea ssp.  Sp: *Goats fed dry feed with 15 g Cd/kg and rats fed on a low Cd diet grew more slowly than control animals with 300 g Cd/kg feed. The goats with a low Cd diet had difficulty in conceiving. **Itai-Itai disease (Japan): the Cd content of river water from a silver mine used to irrigate rice paddies led to increased Cd content in the rice and thus to skeleton deformation and spontaneous fractures in man. Released from metallurgical plants, towns, refuse incineration plants, cigarette smoke, mineral fertilizers and sewage sludge</p>								
Ce	Bac -	Alg -	Fun -	HPI -	An -	S: 50 P: 0.25-0.55 R: 0.5	Slightly toxic	Ce <sup>3+</sup> CeOH <sup>2+</sup>
<p>A: Carya spec.  Sp: See under La</p>								
Cl	Bac +/-	Alg +	Fun -	HPI +	An +	S: 100* P: 0.2-2% R: 0.2%	Rel. untox**	Cl <sup>-</sup>
<p>A: Halophytes such as Chenopodiaceae, Frankeniaceae, Plumbaginaceae, mangroves such as Rhizophoraceae, Verbenaceae  F: Osmolytic function, enzyme activation  De: Wilting and root thickening  Sp: *Very high concentrations in arid and semiarid soils. **Cl<sub>2</sub> and a large number of organochlorine compounds are highly toxic. Apart from the natural emission potential from the ocean, its use in deicing salt for roads can be regarded as a potential danger for soils and waters. Chlorine is a raw material for the production of solvents and is an active substance in bleaches. It is also used for the stabilization and purification of water</p>								

## Appendix 1. Continued.

	Essentiality					Occurrence (mg/kg DW)	Toxicity	Uptake in the form of
Co	Bac +/-	Alg +/-	Fun -	HPI* ?	An +	S: 1-40 P: 0.02-0.5 R: 0.2	Weakly toxic Pl: 0.1-3 mg/l M: 500 mg/d, l	Co <sup>2+</sup> CoCO <sub>3</sub>
<p>A: <i>Clethra barbinervis</i>, <i>Crotalaria cobaticola</i>, <i>Nyssa sylvatica</i>  F: Part of vitamin B<sub>12</sub>, enzymatic  De: Anaemia, vitamin B<sub>12</sub> deficiency, disturbance of nucleic acid synthesis  Sp: Whether Co is essential for higher plants remains unclear, nevertheless it is undoubtedly necessary for the N<sub>2</sub> fixation system of <i>Rhizobium</i> bacteria living in a state of symbiosis with the leguminosae. The addition of slight quantities of Co often leads to improved yields</p>								
Cr	Bac -	Alg -	Fun -	HPI -	An +	S: 2-100 P: 0.2-1 R: 1.5	Toxic* Pl: 1 mg Cr(VI)/l M: 3 g/d, l	Cr(OH) <sub>3</sub> CrO <sub>4</sub> <sup>-</sup>
<p>A: <i>Leptospermum scoparium</i>, <i>Pimelia suteri</i>  F: Insulin intensification, glucose tolerance function  De: Diabetes, increased serum lipids  Sp: *Cr(VI) is about 1000 times more toxic than Cr(III) (basically only Cr(VI) is capable of passing through the cell membrane). In cells Cr(III) is preferentially found in the walls, Cr(VI) in the cell sap, whereas the concentration in the mitochondria and the cell nuclei is comparatively low</p>								
Cs	Bac -	Alg -	Fun -	HPI -	An -	S: 1-20 P: 0.03-0.44 R: 0.2	Rel. harmless	Cs <sup>+</sup>
<p>Sp: Cs<sup>134</sup> released during nuclear fission</p>								
Cu	Bac +	Alg +	Fun +	HPI +	An +	S: 1-80 P: 2-20 mg/l R: 10	Toxic* Pl: 0.5-8 mg/l M: 250 mg/d	CuOH <sup>+</sup> CuCO <sub>3</sub>
<p>A: <i>Aeolanthus biformifolus</i>, <i>Becium homblei</i>, <i>Cryptosepalum maraviense</i>, <i>Elsholtzia haichowensis</i>, <i>Gypsophila patrinii</i>, <i>Lychnis alpina</i>, <i>Polycarpea spirostylis</i>, <i>Silene dioica</i>, <i>Silene vulgaris</i>, <i>Triumfetta welwitschi</i>, <i>Uapaca</i> ssp., <i>Veronica glaberrima</i>  F: Energy metabolism, N metabolism, oxidizing systems, elastin cross-linkage, catalytic function in many redox reactions  De: E.g. grey speck disease of cereals, drying of leaf tips, wilting, spot chlorosis of young leaves, blocking of oxidation (respiration), anaemia, changes in bone formation  Sp: *Released into drinking water from copper pipes</p>								
Dy	Bac -	Alg -	Fun -	HPI -	An -	S: 5 P: 0.025-0.05 R: 0.03	Slightly toxic	Dy <sup>3+</sup> DyOH <sup>2+</sup>
<p>A: <i>Carya spec.</i>  Sp: See under La</p>								
Er	Bac -	Alg -	Fun -	HPI -	An -	S: 2 P: 0.015-0.030 R: 0.02	Slightly toxic	Er <sup>3+</sup> ErOH <sup>2+</sup>
<p>A: <i>Carya spec.</i>  Sp: See under La</p>								

## Appendix 1. Continued.

	Essentiality					Occurrence (mg/kg DW)	Toxicity	Uptake in the form of
Eu	Bac -	Alg -	Fun -	HPl -	An -	S: 1 P: 0.005–0.015 R: 0.008	Slightly toxic	Eu <sup>3+</sup> EuOH <sup>2+</sup>
	A: <i>Carya spec.</i> Sp: See under La							
F	Bac -	Alg -	Fun -	HPl -	An +	S: 10–1000 P: 2–20 R: 2	Toxic* Pl: 5 mg/l M: 20 mg/d	F <sup>-</sup> HF
	A: <i>Acacia georginae</i> , <i>Dichapetalum ssp.</i> , <i>Gastrolobium grandiflorum</i> , <i>Porifera Dysidea crawshayi</i> , human teeth, F: In mammals fluorine strengthens the teeth during development. An excess of fluorine can lead to fluorosis as known from grazing animals in North Africa Sp: *Fluorine is released from the ceramic, cement and brickmaking industry. The resulting dusts and gases containing fluoride can lead to agricultural and forestry damage							
fe	Bac +	Alg +	Fun +	HPl +	An +	S: 0.7–42% P: 5–200 R: 150	Hardly toxic Pl: 10–200 mg/l m: 200 mg/d	Fe <sup>2+</sup> Fe(OH) <sub>2</sub> <sup>+</sup>
	A: Iron bacteria, lichen <i>Acarospora smaragdula</i> , red blood corpuscles F: Chlorophyll synthesis, many iron enzymes, ferritin as the storage and transport form, haemoglobin De: Straw-coloured intercostal chloroses or whitening of young leaves, apical buds suppressed, anaemia, growth reduction, haemolysis							
Ga	Bac -	Alg -	Fun -	HPl -	An -	S: 0.1–10 P: 0.01–0.23 R: 0.1	Rat: 10 mg/d	Ga(OH) <sub>4</sub> <sup>-</sup>
	Sp: Used for antitumorigenic purposes, various medical applications							
Gd	Bac -	Alg -	Fun -	HPl -	An -	S: 4 P: 0.03–0.06 R: 0.04	Slightly toxic	Gd <sup>3+</sup> GdOH <sup>2+</sup>
	A: <i>Carya spec.</i> Sp: See under La							
Ge	Bac -	Alg -	Fun -	HPl -	An -	S: 1 P: 1–2.4 R: 0.01	Hardly toxic (apart from GeH <sub>4</sub> )	Ge(OH) <sub>4</sub>
	Sp: Germanium organic compounds are used as chemotherapeutic agents for bacteria. Spiro-germanium (4.4-dialkyl-4-germacyclohexanone and 8.8-dialkyl-8-germaazaspiro (4.5) decane is used for antitumorigenic purposes							
H	Bac +	Alg +	Fun +	HPl +	An +	S: variable P: 4.1–7.2% R: 6.5%	As D <sub>2</sub> O	H <sub>2</sub> O
	F: Participates in the structure of a large number of organic compounds, supplies reduction equivalents in physiological processes							
Hf	Bac -	Alg -	Fun -	HPl -	An -	S: 6 P: 0.001–1 R: 0.05	Hardly toxic	

## Appendix 1. Continued.

	Essentiality					Occurrence (mg/kg DW)	Toxicity	Uptake in the form of
Hg	Bac -	Alg -	Fun -	HPl -	An -	S: 0.01-1 P: 0.005-0.2 R: 0.1	Toxic* M: 0.4 mg/d	Hg(OH) <sub>2</sub> HgOHCl
A: <i>Minuartia setacea</i> , <i>Betula papyrifera</i> Sp: *Toxicity increases from elemental mercury, ionic mercury to organomercury compounds. Amalgam dental fillings may lead to allergies. Minamata disease: a disease which occurred from 1953-1960 in Minamata Bay, Japan. Water containing methyl mercury had contaminated the food fish. In humans, the disease took the form of serious kidney damage and damage to the immunological system also leading to fatalities.								
Ho	Bac -	Alg -	Fun -	HPl -	An -	S: 0.6 P: 0.005-0.015 R: 0.008	Slightly toxic	Ho <sup>3+</sup> HoOH <sup>2+</sup>
A: <i>Carya spec.</i> Sp: See under La								
I	Bac -	Alg +/-	Fun -	HPl -	An +	S: 1-5 P: 0.07-10 R: 3	Rel. untox.* Pl: 1 mg/l M: 2 mg/d	I <sup>-</sup> IO <sub>3</sub> <sup>-</sup>
A: Red and brown algae, many Porifera, some Coelenterata, <i>Feijoa sellowiana</i> F: The thyroid gland hormone tyrosine De: Goitre formation, cretinism Sp: *Various iodine isotopes are released during nuclear weapons tests and reactor accidents which may become dangerous due to the accumulation of iodine in the thyroid glands of mammals and humans								
In	Bac -	Alg -	Fun -	HPl -	An -	S: 0.2-0.5 P: 0.0005-0.002 R: 0.001	Rat: 200 mg/d, 1	In(OH) <sub>4</sub> <sup>-</sup>
Ir	Bac -	Alg -	Fun -	HPl -	An -	S: ? P: ? R: 0.00001		
Sp: See under Pt								
K	Bac +	Alg +	Fun +	HPl +	An +	S: 0.2-2.2% P: 0.5-3.4% R: 1.9%	Rel. harmless	K <sup>+</sup>
F: Electrochemical, catalytical, enzyme activation De: Deficiency disturbs the water balance (drying of leaf tips), Leaf curling (wilting) on older leaves, root rot								
La	Bac -	Alg -	Fun -	HPl -	An -	S: 40 P: 0.15-0.25 R: 0.2	Slightly toxic Rat: 720 mg/d, 1	La <sup>3+</sup> LaOH <sup>2+</sup>
A: <i>Carya spec.</i> Sp: The lanthanides are not considered to be essential and are only slightly toxic. In environmental specimens they obey the Harkins rule which says that a lanthanide with an odd atomic number occurs in a lower concentration than the directly adjacent lanthanide element with an even atomic number								



## Appendix 1. Continued.

	Essentiality					Occurrence (mg/kg DW)	Toxicity	Uptake in the form of
Li	Bac –	Alg –	Fun –	HPl –	An ?	S: 1–100 P: 0.01–3.1 R: 0.2	Slightly toxic Pl: 30 mg/l M: 200 mg/d	Li <sup>+</sup>
A: Solanaceae in arid climates Sp: Lithium compounds are used to treat manic depressives. Possible essentiality for mammals under discussion								
Lu	Bac –	Alg –	Fun –	HPl –	An –	S: 0.4 P: 0.0025–0.005 R: 0.003	Slightly toxic	Lu <sup>3+</sup> LuOH <sup>2+</sup>
A: <i>Carya spec.</i> Sp: See under La								
Mg	Bac +	Alg +	Fun +	HPl +	An +	S: 500–5000* P: 1000–9000 R: 2000	Hardly toxic	Mg <sup>2+</sup> MgOH <sup>+</sup>
A: Marine algae accumulate 6000–20000 mg/kg DW F: Enzyme component and chlorophyll structure, electrochemical and catalytic functions De: Deficiency causes stunted growth and intercostal chlorosis on older leaves Sp: *Higher Mg contents in the soil arise in the case of rock containing MgCO <sub>3</sub>								
Mn	Bac +	Alg +	Fun +	HPl +	An +	S: 20–3000 P: 1–700 R: 200	Slightly toxic Pl: 1–100 mg/l Rat: 10–20 mg/d	Mn <sup>2+</sup>
A: Ericaceae and Theaceae, Diatomeae <i>coscinodiscus</i> , Porifera <i>Terpios zeteki</i> , Annelida <i>hermione</i> , Ascidiaceae <i>Didemnum</i> and <i>Halocynthia</i> F: Nucleic acid synthesis, photolysis of water during the light reaction of photosynthesis, stabilizes chloroplast structure, metabolism of the mucopolysaccharides, superoxide dismutase, arginase, pyruvate carboxylase, malate enzyme De: Chloroses and necroses on young leaves, defoliation, bone deformation, anaemia, reduced growth								
Mo	Bac +	Alg +	Fun +	HPl +	An +	S: 0.2–5 P: 0.03–5 R: 0.5	Slightly toxic Pl: 0.5–2 mg/l Rat: 5 mg/d	MoO <sub>4</sub> <sup>–</sup>
A: <i>Grindelia fastigiata</i> F: N fixation, P metabolism, Fe absorption and translocation, xanthine oxidase, sulphoxidase De: Disturbed growth and shoot deformation, discoloration of leaf edges, disturbance of fatty acid formation from carbohydrates Sp: Leguminosae require about three times as much Mo as other spermatophytes since N fixation by the symbiotic rhizobia requires Mo								
N	Bac +	Alg +	Fun +	HPl +	An +	S: 2000 P: 1.2–7.5% R: 2.5%	Ecotoxic	NO <sub>3</sub> <sup>–</sup> NH <sub>4</sub> <sup>+</sup>
F: Structure of many organic compounds, many metabolic physiological functions De: Stunted growth or dwarfism, bulky growth and skleromorphosis, premature yellowing of older leaves Sp: *Simple nitrogen compounds today represent an extensive ecotoxicological problem, e.g. the nitrate problem associated with large-scale livestock farming, NO <sub>2</sub> -emissions, N <sub>2</sub> O as a greenhouse gas in the atmosphere								

## Appendix 1. Continued.

	Essentiality					Occurrence (mg/kg DW)	Toxicity	Uptake in the form of
Na	Bac +/-	Alg +/-	Fun -	HPI +/-	An +	S: variable P: 35-1000 R: 150	Rel. harmless	Na <sup>+</sup>
	A: Halophytes, some Chenopodiaceae, Frankeniaceae and Plumbaginaceae, mangroves such as Avicennia, Bruguiera and Rhizophora F: Electrochemical, enzyme activation							
Nb	Bac -	Alg -	Fun -	HPI -	An -	S: 10 P: 0.28 R: 0.05	Slightly toxic	
	A: Ascidian: Molgula manhattensis							
Nd	Bac -	Alg -	Fun -	HPI -	An -	S: 35 P: 0.1-0.25 R: 0.2	Slightly toxic	Nd <sup>3+</sup> NdOH <sup>2+</sup>
	A: Carya spec. Sp: See under La							
Ni	Bac +/-	Alg +/-	Fun -	HPI +/-	An +	S: 2-50 P: 0.4-4 R: 1.5	Toxic** Pl: 0.5-2 mg/l Rat: 50 mg/d	Ni <sup>2+</sup>
	A: Alyssum bertolinii and Alyssum murale, Dicoma ssp., Homalium ssp., Hybanthus floribundus, Pimelia suteri, Planchonela ssp., Psychotria ssp., Rinorea bengalensis, Sebertia ssp. Poriferae Dysidea F: Interaction with iron resorption De: Growth reduction Sp: *For some plants and microorganisms Ni is a component of urease and therefore essential. **Ni(CO) <sub>4</sub> is a highly toxic industrial product							
O	Bac* +/-	Alg +	Fun +	HPI +	An +	S: 49% P: 40-44% R: 42.5%	Toxic in the form of O <sub>3</sub> and peroxide	O <sub>2</sub> CO <sub>2</sub>
	F: Structure of many organic compounds, provides oxidation equivalents in the metabolism Sp: *Lethal for obligate anaerobic microorganisms							
Os	Bac -	Alg -	Fun -	HPI -	An -	S: ? P: ? R: 0.000015	Very toxic in the form of OsO <sub>4</sub>	
	Sp: See under Pt							
P	Bac +	Alg +	Fun +	HPI +	An +	S: 200-800 P: 120-30000 R: 2000	Ecotoxic*	HPO <sub>4</sub> <sup>2-</sup> H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>
	F: Hydroxiapatite for mammals during bone and teeth formation, energy metabolism, phosphorilization, DNA and ATP structure De: Disturbance of reproductive processes (flowering inhibition), bulky growth, dry tips in the case of conifer needles Sp: *Eutrophication of waters, phosphate esters which enter the water as insecticides have a toxic effect on much aquatic life, phosphates are relatively harmless, phosphoric acid esters and PH <sub>3</sub> are very toxic							

## Appendix 1. Continued.

	Essentiality					Occurrence (mg/kg DW)	Toxicity	Uptake in the form of
Pa	Bac –	Alg –	Fun –	HPl –	An –	S: ? P: ? R: ?		
Pb	Bac –	Alg –	Fun –	HPl –	An* ?	S: 0.1–200 P: 0.1–5 R: 1	Toxic Pl: 3–20 mg/l M: 1 mg/d	PbCO <sub>3</sub>
A: <i>Amorpha canescens</i> , <i>Minuartia verna</i> , lichen <i>Stereocaulan pileatum</i> F: *Essentiality for vertebrates under discussion. Pb enters into the environment (currently to a decreasing extent) particularly from the use of tetraethyl lead as an antiknock agent for petrol engines								
Pd	Bac –	Alg –	Fun –	HPl –	An –	S: ? P: ? R: 0.0001	Toxic	
Sp: See under Pt								
Po	Bac –	Alg –	Fun –	HPl –	An –	S: 8–220 Bq/kg P: 8–12 Bq/kg R: ?	Highly toxic for vertebrates	
Pr	Bac –	Alg –	Fun –	HPl –	An –	S: 3–12 P: 0.03–0.06 R: 0.05	Slightly toxic	Pr <sup>3+</sup> PrOH <sup>2+</sup>
A: <i>Carya spec.</i> Sp: See under La								
Pt	Bac –	Alg –	Fun –	HPl –	An –	S: ? P: ? R: 0.00005	Slightly toxic	
Sp: 0.9–2.3 g Pt is contained in three-way catalytic converters. Pt metal and its salts cause allergic contact eczema. Cis-dichloroplatinum(II) complexes are used in cancer therapy. Pt and its family enter into the environment due to natural wear from exhaust catalytic converters in cars. Together with aluminium oxide as the carrier material, these compounds are released into the air in a highly dispersive metallic form as suspended matter and subsequently deposited. The consequences of this are still unclear, particularly since the concentrations of platinum metal naturally occurring in the environment are very low and often cannot be determined exactly								
Ra	Bac –	Alg –	Fun –	HPl –	An –	S: ? P: 0.03–1.6 ppt R: ?	Radioactive*	Ra <sup>2+</sup>
A: <i>Bertholletia excelsa</i> Sp: *Similar chemical behaviour to Ba and Ca, therefore incorporation into the bone substance. 10–20 µg is sufficient to cause bone-marrow depression and myelosarcomas								
Rb	Bac –	Alg –	Fun –	HPl –	An –	S: 10–100 P: 1–50 R: 50	Slightly toxic Rat: 10 mg/d	Rb <sup>+</sup>
Sp: Similarity to K, may replace K at bonding locations, however not in its physiological effect								

## Appendix I. Continued.

	Essentiality					Occurrence (mg/kg DW)	Toxicity	Uptake in the form of
Re	Bac -	Alg -	Fun -	HPl -	An -	S: ? P: ? R: ?		ReO <sub>4</sub> <sup>-</sup>
Rh	Bac -	Alg -	Fun -	HPl -	An -	S: ? P: ? R: 0.00001		
	Sp: Se under Pt							
Ru	Bac -	Alg -	Fun -	HPl -	An -	S: ? P: ? R: 0.00001		
	Sp: See under Pt							
S	Bac +	Alg +	Fun +	HPl +	An +	S: 200–2000* P: 600–10000 R: 3000	Ecotoxic**	SO <sub>4</sub> <sup>2-</sup> HSO <sub>4</sub> <sup>-</sup>
	A: Individual plants of the Cruciferae, <i>Alium</i> spp; sulphur bacteria, vertebrate hair, feathers F: Constitute of amino acids (cysteine and methionine), of coenzymes, acid mucopolysaccharides and sulphuric acid esters De: Very similar to N deficiency, intercostal chloroses of young leaves, premature yellowing of leaves and needles Sp: *Considerably higher contents on gypsum soils. **Influence of anthropogenic SO <sub>2</sub> emissions on 'new' forest damage, soil acidification							
Sb	Bac -	Alg -	Fun -	HPl -	An -	S: 0.01–1 P: 0.1–200 ppb R: 0.1	Toxic* M: 100 mg/d Rat: 10–75 mg/d, l	Sb(OH) <sub>6</sub> <sup>-</sup>
	Sp: *Sb(III) is more toxic than Sb(V)							
Sc	Bac -	Alg -	Fun -	HPl -	An -	S: 0.5c45 P: 0.01–0.2 R: 0.02	Slightly toxic	Sc(OH) <sub>3</sub>
Se	Bac -	Alg -	Fun -	HPl +/-	An +	S: 0.01 P: 0.01–2 R: 0.02	Toxic* Pl: 1–2 mg Se(IV)/l M: 5 mg/d Rat: 1–2 mg/d, l	SeO <sub>3</sub> <sup>-</sup>
	A: Fungus <i>Boletus edulis</i> , individual species from the families of the Compositae, Lecythidaceae, the Leguminosae (e.g. <i>Astragalus</i> ) and the Rubiaceae F: Component of glutathione peroxidase De: Deficiency causes lipid peroxidation, endemic cardiomyopathy and haemolysis in animals and man Sp: *Selenites and selenates are very toxic. The toxicity of As, Hg, Cd, Tl and NO <sub>3</sub> <sup>-</sup> is reduced if Se is taken up at the same time. The toxic effect results from the replacement of sulphur by Se in amino acids							

## Appendix 1. Continued.

	Essentiality					Occurrence (mg/kg DW)	Toxicity	Uptake in the form of
Si	Bac +	Alg -	Fun -	HPI +/-	An +	S: 33%* P: 200-8000 R: 1000	Physically e.g. in the form of asbestos	Si(OH) <sub>4</sub>
	<p>A: Diatoms, radiolarians and siliceous sponges, Sphenopsida, Cyperaceae, Gramineae, Juncaceae  F: Structural component of siliceous skeletons, calcification  De: Growth disturbances, bone deformation  Sp/ *Clearly lower contents on particular soils, e.g. limestone. Organic Si compounds may be highly toxic. Some Si compounds such as Si halogen compounds are corrosive</p>							
Sm	Bac -	Alg -	Fun -	HPI -	An -	S: 4.5 P: 0.02-0.04 R: 0.04	Slightly toxic	Sm <sup>3+</sup> SmOH <sup>2+</sup>
	<p>A: <i>Carya spec.</i>  Sp: See under La</p>							
Sn	Bac -	Alg -	Fun -	HPI -	An* ?	S: 1-20 P: 0.8-7 R: 0.2	Hardly M: 2 g/d	SnO(OH) <sub>3</sub> <sup>-</sup>
	<p>A: <i>Silene vulgaris</i>, Poriferae <i>Terpios zeteki</i>  F: *Sn may possibly be essential for vertebrates  De: Growth disturbances occur in vertebrates, furthermore digestive enzymes are not secreted  Sp: Organotin compounds (e.g. triphenyltin) are used as fungicides, insecticides and bactericides</p>							
Sr	Bac -	Alg -	Fun -	HPI -	An -	S: 20-3500 P: 3-400 R: 50	In the form of Sr <sup>90</sup> *	Sr <sup>2+</sup>
	<p>A: Protozoa <i>Acanthometra</i>, brown algae  Sp: Sr seems to be essential for some organisms. However, this requires further investigation. *Sr<sup>90</sup> is a decay product from nuclear explosions and as a consequence of its similarity to Ca is incorporated into bone substance</p>							
Ta	Bac -	Alg -	Fun -	HPI -	An -	S: 0.5-4 P: <0.001 R: 0.001	Slightly toxic Rat: 300 mg/d, l	
	<p>A: <i>Ascidia Stylea plicata</i></p>							
Tb	Bac -	Alg -	Fun -	HPI -	An -	S: 0.7 P: 0.005-0.015 R: 0.008	Slightly toxic	Tb <sup>3+</sup> TbOH <sup>2+</sup>
	<p>A: <i>Carya spec.</i>  Sp: See under La</p>							
Te	Bac -	Alg -	Fun -	HPI -	An -	S: ? P: 0.01-0.35 R: 0.05	Toxic Pl: 6 mg/l Rat: 1-9 mg/d, l	HTeO <sub>3</sub> <sup>-</sup>
Th	Bac -	Alg -	Fun -	HPI -	An -	S: 9 P: 0.03-1.3 R: 0.005	Toxic	Th(OH) <sub>4</sub> <sup>4- n</sup>

## Appendix 1. Continued.

	Essentiality					Occurrence (mg/kg DW)	Toxicity	Uptake in the form of
Tl	Bac -	Alg -	Fun -	HPl -	An -	S: 0.01-0.5 P: 0.03-0.3 R: 0.05	Toxic Pl: 1 mg/l M: 600 mg/d	Tl <sup>+</sup>
	Sp: Particularly high environmental concentrations in the vicinity of cement factories							
Ti	Bac -	Alg -	Fun -	HPl -	An* -	S: 1500-5000** P: 0.02-56 R: 5	Hardly toxic***	Ti(OH) <sub>4</sub>
	F: *Although Ti is not regarded as essential for plants nevertheless it may play a positive role in cereal growth and for N <sub>2</sub> fixation by Leguminosae. ** 15% in the upper layers of lateritic soils. The measured Ti content during plant analysis may be used as an indicator of contamination by soil particles. *** Due to its grain size of 20 μm, the titanium dioxide pigment is classified as dust pollution.							
Tm	Bac -	Alg -	Fun -	HPl -	An -	S: 0.6 P: 0.0025-0.005 R: 0.004	Slightly toxic	Tm <sup>3+</sup> TmOH <sup>2+</sup>
	A: <i>Carya spec.</i> Sp: See under La							
U	Bac -	Alg -	Fun -	HPl -	An -	S: 0.01-1 P: 0.005-0.06 R: 0.01	Highly toxic Rat: 36 mg/d, l	UO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> <sup>-</sup>
	A: <i>Coprosma arborea</i> , <i>Uncinia leptostachya</i> , some corals							
V	Bac -	Alg +/-	Fun -	HPl +/-	An +/-	S: 10-100 P: 0.001-10 R: 0.5	Toxic P: 10-40 mg/l Rat: 0.25 mg/d	H <sub>2</sub> VO <sub>4</sub> <sup>-</sup> HVO <sub>4</sub> <sup>-</sup>
	A: Fungi: <i>Amanita muscaria</i> , <i>Astragalus confertiflorus</i> , ascidians F: Inhibition of cholesterol synthesis De: Growth reduction, changes in lipid metabolism, fertility disturbances Sp: Some sea cucumbers, in isolated cases molluscs and generally ascidians contain high V concentrations. Some species of ascidians have a vanadium protein complex in their blood and other species a pyrrole complex in the green blood corpuscles, the vanadocytes. The general function of vanadium is unclear							
W	Bac -	Alg -	Fun -	HPl -	An -	S: 1.5 P: 0.0005-0.15 R: 0.2	Slightly toxic Pl: 10 mg/l Rat: 30-50 mg/d, l	WO <sub>4</sub> <sup>-</sup>
	A: <i>Pinus cembra</i> Sp: The physiological effect of tungsten is as an antagonist to molybdenum where the replacement of Mo by W in the corresponding enzymes (e.g. xanthine oxidase) generally leads to a drop in activity							
Y	Bac -	Alg -	Fun -	HPl -	An -	S: 40 P: 0.15-0.77 R: 0.2	Slightly toxic	Y(OH) <sub>3</sub>
	A: Poriferae <i>Melithoca spp.</i> , <i>Carya spp.</i>							

## Appendix 1. Continued.

	Essentiality					Occurrence (mg/kg DW)	Toxicity	Uptake in the form of
Yb	Bac -	Alg -	Fun -	HPl -	An -	S: 3 P: 0.015-0.030 R: 0.02	Slightly toxic	Yb <sup>3+</sup> YbOH <sup>2+</sup>
	A: <i>Carya spec.</i> Sp: See under La							
Zn	Bac +	Alg +	Fun +	HPl +	An +	S: 3-300 P: 15-150 R: 50	Toxic Pl: 60-400 mg/l M: 150-600 mg/l	Zn <sup>2+</sup> ZnOH <sup>+</sup> ZnCO <sub>3</sub>
	A: <i>Armeria maritima</i> subsp. <i>halleri</i> , <i>Minuartia verna</i> , <i>Silene vulgaris</i> , <i>Thlaspi alpestre</i> , <i>Viola tricolor</i> var. <i>calaminaria</i> F: Chlorophyll formation, enzyme activator, energy metabolism (dehydrogenases), protein degradation, formation of growth substance (IES), transcription De: Growth inhibition, whitish green discoloration of older leaves, fructification disturbances Sp: Toxic symptoms in humans are sexual immaturity, skin lesions and grey hair. Soils rich in Zn are termed 'calamine soils' and support 'calamine flora'							
Zr	Bac -	Alg -	Fun -	HPl -	An -	S: 1-300 P: 0.3-2 R: 0.1	Slightly toxic Rat: 250 mg/d	Zr(OH) <sub>n</sub> <sup>4-n</sup>

## Appendix 2

Estimated annual production of individual elements for the year 2000 (if not specified otherwise) and examples of their technical application. The data used in appendix 2 were extracted from Bowen 1979; Council of Environmental Quality 1980; Kabata-Pendias & Pendias 1984; Merian 1991; Nriagu 1988 and Streit 1991.

Sym- bol	Estimated annual produc- tion in the year 2000 (in 1000 t)	Examples of technical application
Ac		Ac is used as a radioactive source to generate alpha radiation.
Ag	12	Ag is used for photographic material, for electric controllers and conductors, for coins, medals, jewellery, silverware, alkali batteries, mirrors, catalysts, hard alloys and silver-plated objects.
Al	60000	Aluminium is applied, for example, in producing sheet metal, wires and alloys. Al salts are used in sewage plants to precipitate phosphate.
As	51	Metallic arsenic is used as an alloying element to increase hardness. Copper arsenide, $\text{Cu}(\text{AsO}_2)_2$ , is effective as an insecticide and fungicide.
Au	2	Gold is applied in electroplating, electronics and jewellery production.
B	1000 (in 1974)	Boron is a component of alloys. Boron nitrides (in the diamondlike modification) are important abrasives. Boron compounds are used in the glass, ceramic and enamel industry (particularly borax and boric acid) and also serve as fertilizers and pesticides.
Ba	5000	Barium sulphate is used in X-ray diagnostics as a contrast medium, barium carbonate is applied for waste water purification and as a rat poison.
Be	15	Be is used for X-ray windows. Alloys of Be with Cu, Al, Ni, Co and Fe increase hardness, temperature- and corrosion stability. Also found in clock springs, surgical instruments, electrical engineering (as electric insulators) and in aerospace applications.

## Appendix 2. Continued.

Sym- bol	Estimated annual produc- tion in the year 2000 (in 1000 t)	Examples of technical application
Bi	6	Bi preparations (bismuth oxide chloride and other salts) are used for cosmetic articles and as soluble salts for pharmaceuticals. Bi is used for easily fusible alloys and also to silver mirrors as well as in battery cathodes, semiconductors and catalysts.
Br	35	Bromium and its compounds are applied as antiknock agents, as fumigants, preservatives, as insecticides, flameproofing agents and in the production of pesticides, dyes, pharmaceuticals and photochemicals.
C	$6 \times 10^6$	Carbon in its elemental form (diamond or graphite) or in the form of its compounds is used in a large number of technical processes, particularly as an energy carrier.
Cd	20	Production of Ni/Cd batteries, used for corrosion control, for pigments and as a plastic stabilizer.
Ce	0.3 (1979)	Cerium oxides are important constituents of self-cleaning ovens, the element also serves as a glass polishing agent (see also La).
Cl	81000 (1979)	Cl is a basic material for the production of solvents and an active substance in bleaches. It is applied for the sterilizing and conditioning of water (chlorination).
Co	30	Co is utilized for hard alloys, to harden tungsten carbide and as a catalyst. Furthermore, it is also a constituent of glasses, pottery, and of blue and green pigments.
Cr	3750	Cr is used in metallurgy to prevent rust and as basic material for the production of paints. Furthermore it is also applied for catalysts, in tanneries and for the impregnation of wood.
Cs	0.03	Utilized in photocells and as a solid rocket propellant ( $\text{CsBH}_4$ ). CsCl is used in electric bulbs and lamps, $\text{Cs}_2\text{CO}_3$ as a catalyst and for the production of cathode material.



## Appendix 2. Continued.

Sym- bol	Estimated annual produc- tion in the year 2000 (in 1000 t)	Examples of technical application
Cu	12000	50% of Cu applications are in electrical engineering. Also used for alloys, water mains, roofing, household goods and coins. $\text{Cu}^{2+}$ in the form of copper sulphate is applied in agriculture as an additive to green fodder in the case of Cu deficiency, in various compositions as a fungicide or bactericide, and as an algicide and molluscicide in water.
Dy		Dy is occasionally applied in nuclear engineering (see also La).
Er		Er is applied in alloys, in nuclear engineering and to colour glasses and enamel (see also La).
Eu		Eu serves as a neutron absorber, furthermore also as an activator in scintillation crystals, as a material in lasers and colour television picture tubes (see also La).
F	3500	Fluorine is released from the aluminium, ceramic, cement and brick-making industry. The resulting dusts and gases containing fluoride may cause the fluoride contents of soils in the vicinity of such industrial areas to rise dramatically and lead to agricultural and forest damage.
Fe	$1 \times 10^6$	Fe is applied as a construction material and for many special purposes. Relatively small quantities of Fe oxides and Fe salts are used as paint pigments or to precipitate water impurities in the so-called third purification stage and thus end up in the discharge flow.
Ga	0.015 (1974)	Gallium is a byproduct of aluminium production. It is primarily applied in the semiconductor industry. Gallium arsenide can be found in solar cells, in various telecommunication sectors and in supercomputing.
Gd		Gd is used for high-temperature alloys, superconductors, magnets and electronic components (see also La).
Ge	0.2	Ge is applied for optical components such as lenses, prisms and windows in infrared spectroscopy. Ge is also used as a catalyst, as an alloying element and in semiconductor technology.
H		Hydrogen in its elemental form or in the form of its compounds is utilized for a wide range of technical processes.

## Appendix 2. Continued.

Sym- bol	Estimated annual produc- tion in the year 2000 (in 1000 t)	Examples of technical application
Hf	0.0013 (1974)	Hafnium is applied for control rods in nuclear reactors, as a filling for flash bulbs and for alloys.
Hg	14	Application in scientific instruments (thermometers, barometers), electrical equipment, dental fillings.
Ho		(See under La).
I	7 (1974)	Iodine is used in the chemical industry (e.g. as a catalyst and stabilizer, paint industry), in photography and medicine (tincture of iodine, X-ray contrast medium, iodine tablets).
In	0.06	Used for alloys, in the semiconductor industry, for special coatings and for fusion treads. $\text{InCl}_3$ is used in the manufacture of fluorescent lamps.
Ir		Ir is utilized for hard platinum alloys, for contacts and fountain pen nibs.
K	18500 (1979)	Used for alloys and organic synthesis. Soluble potassium salts are used as a fertilizer.
La	0.3 (1979)	Used in alloys and as an additive in intensive light sources. Lanthanum oxide is added to glasses as a stabilizer to combat base influences. The lanthanides are used in industry as catalysts, for mineral oil cracking, as luminescent material for colour TV sets and as additives for Hg and fluorescent lamps. They are also employed to improve light spectra, for special glasses, permanent magnets and as control rods for nuclear fuel rods.
Li	33	Used in alloys (e.g. in the production of wheel bearings), a component of electrodes and lubricating greases, reactor coolant. $\text{LiH}$ is also used as a reactor fuel and for drying, condensation and reduction agents, $\text{LiOH}$ as an 'air purifier' and $\text{LiClO}_4$ as rocket fuel.
Lu		Lu is used as a catalyst (see also La).
Mg	242	Constituent of many alloys, fertilizers.

## Appendix 2. Continued.

Sym- bol	Estimated annual produc- tion in the year 2000 (in 1000 t)	Examples of technical application
Mn	18000	Mn is used in steel production to bind oxygen and sulphur, and also in alloys and batteries. Of the organic compounds, the fungicide manganese-ethylene-bis-dithiocabamate and the antiknock agent methylcyclopentadienyl-manganese-tricarbonyl should be mentioned.
Mo	130	Molybdenum is applied in steel production, as well as in pigments, catalysts, lubricants and in flameproofing agents.
N	$120 \times 10^3$ (1979)	N <sub>2</sub> serves as an inert protective gas for welding and is employed in semiconductor production, for deep freezing of food, to displace air from partially filled fuel tanks and as a propellant in aerosol sprays and fire extinguishers. Liquid N <sub>2</sub> is an important coolant. In largescale manufacturing N in an important raw material for the synthesis of compounds containing nitrogen (N oxides, amides, cyanides, nitrides etc.).
Na	53000 (1979)	Used to produce antiknock agents, in metallurgy, for gas-discharge lamps, in fast breeders and solar power stations as a coolant, sodium salts used as fertilizers (e.g. sodium nitrate and sodium molybdate).
Nb	5 (1979)	Nb is used for alloys. It furthermore also serves as a construction material in space capsules, for welding stainless steels and as a material for fuel rod claddings.
Nd		Nd is utilized to colour glass and enamel and as a laser material (see also La).
Ni	1500	Ni is employed in many Ni alloys (kitchen appliances, coins, jewellery, turbines etc.), furthermore as Ni/Cd accumulators and in catalysts. Nickel tetracarbonyl occurs as an intermediate product in nickel purification and is also used for production processes.
O	$23 \times 10^6$	Oxygen in its elemental form or in the form of its compounds is used for a wide range of technical processes.
Os		Os is used for very hard alloys, for pen nibs, bearings, contacts and also for staining in microscopy.

## Appendix 2. Continued.

Sym- bol	Estimated annual produc- tion in the year 2000 (in 1000 t)	Examples of technical application
P	11200 (1979)	The major proportion of technically produced phosphorus products are used for phosphoric acids and phosphates (e.g. for detergents). Further possibilities of applying P are copper phosphide, friction surfaces on match boxes (red P), military incendiaries and semiconductors.
Pa		
Pb	5000	Pb is used in the accumulator industry, for cable coatings, die castings and antiknock agents.
Pd		Used as a catalyst, in dental prostheses and for jewellery alloys.
Po		Radioactive, therefore no general application.
Pr		Applied in electrodes for arc lamps (see also La).
Pt	0.2 (all Pt metals) (1991)	Used as a catalyst, also for crucibles, electrodes and articles of jewellery. In the form of the cis-dichloro-platinum (II) complex it is used in medicine for cancer therapy.
Ra		Previously used in the clockmaking industry (dial illumination) and in radiotherapy, today used together with beryllium as a source of high-energy neutrons.
Rb	0.003	Rb is utilized in semiconductor technology and as a material for photocathodes, rubidium carbonate is used to manufacture special glasses.
Re	0.014	Re is used for heating filaments, thermocouples, fountain pen nibs, filaments in flashlights and as a catalyst.
Rh		Rh is used for various alloys and, for example, is processed into catalysts, heating spirals, thermocouples and also used in jewellery.
Ru		Ru serves as a catalyst and is also used for alloys.
S	$120 \times 10^3$ (1979)	The major fraction is processed in sulphuric acid production, a small fraction is used in elemental form for vulcanization and the manufacture of matches, fungicides, paints, gunpowder and medical preparations.

## Appendix 2. Continued.

Sym- bol	Estimated annual produc- tion in the year 2000 (in 1000 t)	Examples of technical application
Sb	100	Used in the semiconductor industry as an alloy component, in rubber additives, in pigments and paints.
Sc		Sc is released during uranium smelting. It is used in nuclear engineering and as an additive for light sources.
Se	2	Selenium dioxide is used for the glass industry and for electroplating, selenites also for the glass industry and as a feed additive. Cadmium selenide is applied in semiconductor production.
Si	$380 \times 10^3$ (1979)	In its elemental form Si is almost exclusively used as a semiconductor. Si compounds are major constituents of glass, porcelain, earthenware and cement. SiC is a crystalline solid of great hardness and strength.
Sm		Sm is utilized as a neutron absorber in nuclear reactors, in permanent magnets and also as a catalyst (see also La).
Sn	300	Sn is as a coating for sheet iron (corrosion protection, manufacture of tin cans). Organotin compounds (e.g. triphenyltin) serve as fungicides, insecticides and bactericides and are also used as PVC and PCB thermal stabilizers.
Sr	120	Used to refine alloys.
Ta	0.5 (1979)	Ta is utilized for electric capacitors and for lining chemical reactors. It is a component of steel alloys. Cutting tools often contain tantalum carbide.
Tb		Tb is applied in lasers, fluorescent materials and in high-temperature fuel cells (see also La).
Te	0.25	Tellurium is added to steel, lead alloys etc. It is also used in photography and medicine.
Th	0.7 (1984)	$^{232}\text{Th}$ is used in breeder reactors as a fertile material to produce $^{233}\text{U}$ . $\text{ThO}_2$ is applied in the production of crucibles, for heating conductors and as a catalyst for organic syntheses. $\text{ThC}_2$ (thorium carbide) is utilized as a nuclear fuel in nuclear power stations.

## Appendix 2. Continued.

Sym- bol	Estimated annual produc- tion in the year 2000 (in 1000 t)	Examples of technical application
Tl	0.03 (1984)	Used for alloys, low-temperature thermometers, in electronics and for special glasses; $\text{Tl}_2\text{SO}_4$ is used as rat poison.
Ti	1800	Ti is used for titanium dioxide pigments in the production of oil-based paints, plastics, rubber, paper, ceramics, fibres, printing inks, cosmetics and foodstuffs.
Tm		
U	250	Uranium is primarily utilized as a fuel in nuclear reactors and to breed plutonium and other transuranic elements. $^{235}\text{U}$ serves as bomb material and as an additive to natural uranium for nuclear fuel rods.
V	35	V is mainly used for steel production. Vanadium pentoxide serves as a catalyst in technical processes.
W	47	Tungsten is used for the production of hard metals, for electrodes, coiled filaments, heating elements and as a contact material for electric switches.
Y		Yttrium is applied for the red components in the picture tubes of colour TV sets and for alloys. Furthermore, in the form of barium yttrium cuprates it is suitable for high-temperature superconductors.
Yb		Ytterbium is applied as an alloying element (see also La).
Zn	11000	In its metallic form Zn is mainly used as corrosion protection for electroplating in iron and steel production. Zinc oxide is used, for example, for catalysts and pigments; zinc bacitracin is used as a growth-promoting agent in pig and poultry breeding. Various zinc salts serve as insecticides and fungicides.
Zr	500	Zr is a material applied in aerospace and reactor technology. Zr compounds are also used to impregnate textiles, in leather tanning and in the glass and ceramics industry. $\text{ZrO}_2$ is used as an abrasive, a white pigment for porcelain and for fireproof apparatus.

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