

### CETEM

# **Tecnologia Ambienta**

## Instrumental Multielement Analysis in Plant Materials - A Modern Method in Environmental Chemistry and Tropical Systems Research

**Bernd Markert** 

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### **PRESENTATION**

The problem of environmental chemical analysis is of paramount importance to those who devote their lives to the study of the effects of the several elements and their compounds in the environment.

However, although important, this subject is far from an optimal solution. Solutions are sought for, almost, in every given case!

This article of Prof. Markert addresses to the possibilities of utilizing instrumental multielement methods to answer questions that are of concern to the environmentalist.

Rio de Janeiro, May, 1995.

Roberto C. Villas Boas Director

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### **ABSTRACT**

This paper describes possibilities of using instrumental multielement methods to answer various ecological guestions. Emphasis is placed on the ecosystem-related approach and thus comparison of various ecosystems and compartments of these. The basis for this is a project by the International Union of Biological Sciences (IUBS) aimed at establishing "element concentration cadasters in ecosystems" (ECCEs). In principle. the intention is to collect data on the worldwide distribution of individual elements and element species in various ecosystems. Synthetic reference systems (reference plant, freshwater etc.) in the form of chemical fingerprints can prove important aids to chemical characterization of many different kinds of environmental specimens. From the point of view of both toxicology and nutrient physiology such a characterization of ecosystems is expected to provide important information on the concentrations, effects and reactions of individual elements in different systems. Interest has so far been focused mainly on data from the northern hemisphere, but from the biogeo-chemical viewpoint the scope urgently needs to be extended to cover tropical and subtropical systems.

### Keywords

: environmental, chemical analysis, multielement methods

### 1. INTRODUCTION

In the early 1980s the application of instrumental multielement techniques to geological, biological, ecological and medical questions opened up fields of scientific work which, as they continued to develop, provided a multitude of new insights in the sphere of modern research (BOWEN, 1979; KOVACS et al., 1990, 1993; LIETH and MARKERT, 1988, 1990; MARKERT, 1993 a; SANSONI, 1985, 1987; ZEISLER et al., 1988). The field of "biogeochemistry", for example, could not have been opened up without efficient methods of instrumental analysis (ADRIANO, 1992). At the centre of interest are questions of nutrient physiology and ecotoxicology as well as problems of pollutant minimization (FÖ*RSTNER*, and disposal FRANKENBERGER and KARLSON, 1992).

Analysis of the inorganic composition of our environment has special priority, for at the ecotoxicological level elements such as lead, cadmium, arsenic and mercury have played an important role for years (NRIAGU and PACYNA, 1988). Moreover, in respect of the physiology of metabolism, many chemical elements are known to be of essential significance especially at the trace and ultra-trace level (BAKER, 1981; BROOKS, 1993; DAVIES, 1992; ERNST, 1993; LEPP, 1992; SALOMONS and FÖRSTNER, 1984; THORNTON, 1990; VERRLEIS, 1993). This has already been well investigated for elements such as cobalt, nickel, chromium, molybdenum and selenium. The continuing development of instrumental multielement techniques, resulting especially in lower detection levels, better reproducibility and greater accuracy of the measured signal, now makes it possible to determine the concentration of almost all the 88 naturally occurring elements in any matrix.

The earth's crust may be regarded as a natural reservoir for all the chemical elements of the biosphere (KABATA PENDIAS and PENDIAS, 1992). But a remarkable feature is that 99 % of the total mass of the earth's crust consists of only 8 of the 88 naturally occurring elements. It is made up of 46.4 % oxygen, 28.15 % silicon, 8.32 % aluminium, 5.63 % iron, 4.14 % calcium, 2.36 % sodium, 2.33 % magnesium and 2.09 % potassium. Of the 8 most common elements of the earth's crust, oxygen is the only non-metal. The remaining 80 elements in the periodic table account for less than 1 % of its structure (MARKERT, 1992 and 1993 a).

The greater part of the fresh weight of living plant organs, i.e. those with an active metabolism, consists on average of 85 - 90% water. The solid matter of the plant body consists mainly of the following elements: carbon (44.5 %); oxygen (42.5 %); hydrogen (6.5 %); nitrogen (2.5 %); phosphorus (0.2 %); sulphur (0.3 %) and the alkaline and alkaline-earth metals potassium (1.9 %), calcium (1.0 %) and magnesium (0.2 %).

If the average element concentrations in the earth's crust and the dry solids of plants are plotted on a graph against increasing atomic mass as in Figure 1, the initial result is a confused picture; but this does show once more that the bulk of organic life consists chiefly of non-metals, in contrast to the earth's crust. A more interesting picture is Figure 2, in which the molar masses of individual element concentrations in the plant body have been plotted against the molar masses of average single element concentrations in the earth's crust. Most of the element correlations are to be found along the bisector of the angle between the two concentration axes. This shows on the one hand that the extraterrestrial origins of the elements are reflected both in the earth's crust and in the living biomass, and on the other hand that some elements have acquired a special significance in the process of evolution and especially in the biological life of today. These are the elements shown in Group I of Figure 2, namely C, H, O, K, Ca, Si, Na, Fe, P, S, N, Mn, B, Zn, Cu, Ni, Cr, Co, Cl, V, F, Rb, Sr, Ba, Ti and Al. All but the last five have an essential function at least in certain groups of organisms; that is, they are necessary for the life of these organisms. The last five elements - Rb, Sr, Ba, Ti and AI - are also assumed to have

an essential function, but we are unable to define it precisely at present. Some of the elements in Group II are known to have essential functions (I, Mo, Se, and Sn), but they are characterized by a high degree of toxicity, in most cases even at low concentrations. They include most importantly the heavy metals Pb, Cd, As, Tl, Hg etc. Group III consists of elements that have not been able, in the course of evolution, to break away from their passive role in the earth's crust and integrate themselves as active components of organismic life. The most important members of this group are the lanthanides and the platinum metals.

This concept of a selection of chemical elements enabling organic life, based on evolutive development, led to the establishment of a first Biological System of Elements (BSE) which is shown in Figure 3. This Biological System of Elements, originally made out only for glycophytic, terrestrial plants, draws on individual parameters relating to the essentiality and mode of uptake of individual elements and their ability to correlate with each other (MARKERT, 1994 c). It is assumed within the BSE that the elements hydrogen and sodium played a very special role in the development of terrestrial life. This can be seen from their "extraordinary" position outside the periodicity of the BSE. As a structural element of carbohydrates, fats and proteins, an electron donor in redox and thus respiration processes and as a pH regulator, hydrogen may possibly be the chemical element that played the decisive part in the development of aerobic life. Similar element constellations have now been found for halophytes, so that the establishment of a comparable BSE may be expected for these too.

The work described above was only made possible by the advent of a method of instrumental analysis that yielded accurate and reproducible results at all the stages of analysis (Figure 4). That this progress towards accurate results in environmental analysis was not easy - nor is it still! - is illustrated by the words of an outstanding analytical chemist, the late Professor Dr. H. W. Nrnberg, in 1984: "It is evident that competent and efficient

analytical chemistry is a key factor in accurate and reliable assessment of the environmental load, especially as a prerequisite for sound ecotoxicology. It is the analyst's task to conduct it with skill and inspiration. But in this connection the enthusiasm for environmental issues that is pervading many branches of research is also fraught with special risks. These are the ignorance and naivety so often observed in the face of the difficulties to be overcome when carrying out the necessary highly skilled analysis of inorganic environmental chemicals. Many institutions without analytical expertise are starting to buy expensive instruments and indulge in environmental analysis. So we have to expect that in the next few years a glut of false results will be produced that will swell the amount of inaccurate data that already exists. Since the accurate results will then be in the minority there is a danger that for the time being they will simply be drowned in this flood of incorrect data. Severe setbacks of an ecological, ecochemical, social and economic nature may well be the grave long-term results of such an abortive development".

It is true that there has been a meteoric increase in the amount of equipment acquired in recent years. Nowadays routine analytical methods are available for quite a number of elements, as Figure 5 shows. In many cases the estimation of errors from sample preparation to instrumental measurement (Figure 4) can now be carried out satisfactorily by using certified standard reference materials or independent methods, although there is still a great need for new reference materials for quite a number of individual elements and matrices. A much more difficult task is to develop satisfactory methods of sampling and integrate these in an overall concept (DJINGUVA and RULEFF, 1993; ERNST, 1994; FRÄNZLE, 1994; JAYASEKERA, 1993; KABATA-PENDIAS at al., 1991; keune ET AL., 1991; MARKERT, 1994; ROTH, 1992; STEINNES, 1993; WAGNER, 1993; WILKEN, 1992).

### 2. THE IUBS / ECCE PROJECT

In many cases investigations into element patterns and distributions only make sense at ecosystem level, as Figure 6 aims to show. In an ecosystem the paths and whereabouts of the elements may be influenced in a specific manner by organismic activity, for example by selective uptake and accumulation. Elements that occur together may have a positive and/or negative effect on their transportation or accumulation in the organism (MARKERT, 1992, 1993 a). It may be possible to explain antagonistic element behaviour by competition for the same binding site in the organism. Interactions may be assumed to exist between organismic activity and flow rates and flow patterns of the elements through the various components and compartments of an ecosystem which can only be interpreted accurately if all the elements are included in the analysis (LIETH and MARKERT, 1988, 1990). In the case of most elements and ecosystems the nature and extent of these mutual influences doubtless depends on abiotic factors such as the weather. Flow rates and flow patterns therefore vary with these factors. This account when interpreting must always be taken into ecochemical data. It means that the results are characteristic of the constellation of factors under which sampling was carried out (Figure 4).

The following are possible approaches to interpreting the data, depending on which parts of an ecosystem are investigated, how often sampling takes place and what opportunities there are of comparison with other ecosystems of the same kind (Figure 6):

- a) If the system components and compartments analyzed are directly successive stations in the flow of substances, conclusions on the following can be drawn from the results of a single multielement analysis:
  - The concentrations in which individual elements occur:

- Whether and to what extent individual elements occur in correlation in the samples analyzed;
- Whether the samples show accumulative, indicative or rejective behaviour for certain elements.
- b) If a multielement analysis is carried out for a certain constellation of factors in each of several ecosystems of the same kind (characterized, for example, by similar soil conditions and vegetation) which are subject to different inputs of elements, a comparison of the data gives a first indication of how variously similar ecosystems may react to different inputs of substances. Not only do mere changes in concentration have to be taken into account; just as important are modifications of the accumulative behaviour of certain plant species, shifts in element correlations etc. Traditionally, special attention is given to elements known to be of ecotoxicological significance.
- c) When compared with systems that have different vegetation and different soil conditions the results of multielement analyses for a constellation of factors recognized to be characteristic of a particular ecosystem form a reliable basis (possibly with different data) for an analysis of cause and effect (MARKERT, 1992, 1993 a). This provides information on:
- Whether, to what extent and under what conditions the element correlations in the individual plant samples change;
- Whether, to what extent and under what conditions changes in accumulative behaviour can be traced back directly to different soil conditions or plant-specific element patterns;
- Under what constellations of factors and to what extent changes in concentrations are observed.

In particular such a comparison may include systems in different climatic zones. Comparisons between tropical and European virgin forests, or between South American secondary eucalyptus forests and Central European spruce monocultures, are likely to produce interesting results directly relevant to the market economy.

d) If we compare the results of multielement analyses conducted over a lengthy period on similar ecosystems differing only in respect of their input of substances, we may be able to draw conclusions concerning the long-term stability of the systems. Investigations of this kind are being carried out in the context of environmental specimen bank projects, especially in Germany and the USA (ROSSBACH et al., 1992).

The test plan illustrated in Figure 6 shows that multielement analyses of ecosystems must not be regarded as synonymous with mere measuring of element concentrations. The validity and interpretability of concentration data within a series of measurements should always be seen in relation to the specific question to be answered and the particular constellation of parameters. Since August 1991 the International Union of Biological Sciences (IUBS) has been supporting a worldwide multielement programme with the title "Element Concentration Cadasters in Ecosystems" (ECCE). The organizational structure of IUBS / ECCE is shown in Figure 7. The objectives of the long-term programme may be formulated as follows:

### a) Biological objectives

- To establish "element concentration cadasters" of the most common plant species in a forest ecosystem in the form of chemical fingerprints (concentration aspect);
- To establish basic data for a natural ecosystem and determine "natural" baseline concentrations, preferably of elements that have rarely been investigated in the past (concentration aspect);

- To discover interelement relationships and other ways in which plant organisms conform to definite laws (correlation aspect);
- To determine the ability of different plant species to select single elements or groups of elements in the periodic table and to discover possible accumulation properties (accumulation or rejection aspect);
- To use plant systems for monitoring pollutants in ecosystems over lengthy periods of time (indication aspect).
  - b) Analytical objectives
- To improve representative sampling and develop individual environmental sampling programmes;
- To optimize sample preparation techniques (especially washing, homogenizing, drying, decomposition and ashing);
- To use and compare different multielement methods suitable for chemical characterization of environmental samples in respect of the reproducibility, accuracy and concentration dependence of the analytical data.

### 3. PRESENTATION AND EVALUATION OF THE DATA

### 3.1 Synthetic Reference Systems

One of the problems of inorganic-chemical analysis that receives far too little attention is the manner in which the results are presented. The difficulties lie in the large amount of individual data and the distribution of these data over concentration ranges that are usually between 106 and 10-9 mg/kg. In the majority of cases the data are presented in the form of complicated tables, and these generally only permit "element to element" comparisons. An example is Table 2, that shows a multielement comparison of seven plant species in two forest ecosystems in Germany and Russia.

A first approach to establishing a reference system for plants to which all the multielement data produced worldwide could in future be related was the development of a "reference plant" on the lines of the "reference man" created back in the 1960s. The average chemical composition of this plant is shown in Figure 8. In establishing this reference plant it did not very much matter whether it was a moss, a fern, a flowering plant or a tree. The aim was rather to specify its inorganic-chemical composition in order to enable a comparison of multielement data acquired by chemical analysis from all manner of investigations conducted on plants. Like the data for the element composition of reference man, the data for the reference plant shown in Figure 8 will often have to be modified. One reason is that our knowledge of the chemical composition of plant bodies will increase enormously in future as a result of further multielement analysis; another is that the data shown here is not adequately backed up by statistics.

By normalizing against the values of the reference plant and depicting the positive and negative deviations of the individual plant species from the standard values of the reference plant as percentages on a graph it was possible to produce so-called "chemical fingerprints". Figure 9 is such a fingerprint for Vaccinium vitis-idaea (red whortleberry). In this paper it is not possible to go into details of the possibilities offered by chemical fingerprinting. These are adequately described in the literature (e.g. MARKERT, 1993 a; ROSSBACH, 1992; ZEISLER et al., 1988). Let us only say this much here by way of a summary: through normalization against the reference plant, inorganic fingerprints permit a direct comparison of individual plant species. A great advantage is that they enable comparisons over any number of orders of magnitude of individual concentration ranges; such comparisons plainly indicate not only an accumulation of single elements but a reduction in these as well. If the detection limit of analysis is reached or some element concentrations are missing because they have not been determined, this does not affect the comparability of individual fingerprint graphs. Fingerprint graphs make it possible, in general, to demonstrate any marked characteristics of individual plant species, thus enabling these plants to be identified by their typical element composition. Comparisons of individual species make it possible to qualify certain chemical distribution patterns and recognize kinships. The success of this chemical system depends very much on "proper" representative sampling of the individual plant species and "proper" overall conduct of analysis.

Similar reference systems have since been devised for other environmental compartments as well. Figure 10 shows such a system for fresh water. Where sampling is sufficiently representative and the constellation of factors is known, this should give rise to totally new ways of comparing both stagnant and flowing waters. Initial investigations have recently started in South American systems (MARKERT and GELLER, 1994).

The data described above will now permit global calculations leading to model statements on the occurrence and available resources of individual elements in the different compartments and in the ecosystems themselves. In this way the total content of chemical elements in the vegetable biomass of the earth was recently calculated (MARKERT, 1992) - Table 1. This calculation

revealed, for example, that a total of 90 tonnes of platinum is bound in the overall plant biomass of the earth. These figures are subject to an error factor of anything up to two or three orders of magnitude because of elements of uncertainty in analysis, inadequate statistical backup and insufficient quantities of data on which to base them, especially in tropical and subtropical regions (ABRAD and WASSERMAN, 1993; DURSMA, 1993; GOLLEY et al., 1978; JAYASEKERA, 1993; LACERDA and BARCELLOS, 1993; MÜLLER, 1993; PAYNE, 1986; PEDRUZO et al., 1993; ZAUKE et al., 1992). Nevertheless, this material offers an initial, fundamental basis on which to calculate global ecosystem models.

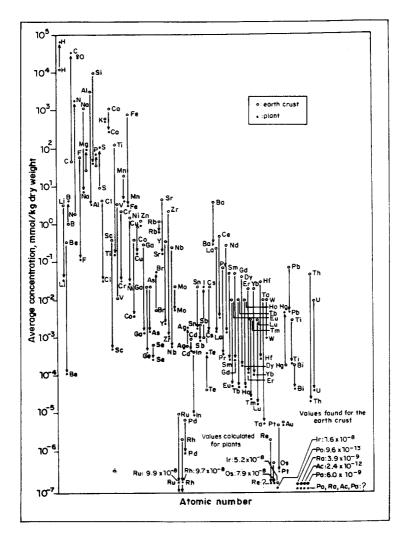


Figure 1 - Average concentrations (in mmol/kg dry weight) of all elements (except the noble gases) occurring naturally in the earth's crust and in plants, plotted according to increasing atomic numbers.

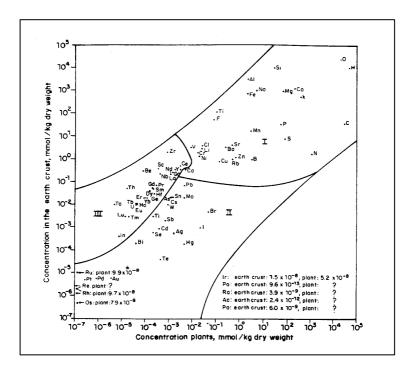


Figure 2 - Average concentrations of individual chemical elements in plants, plotted against the average element concentrations in the earth's crust. All figures in mmol/kg dry weight.

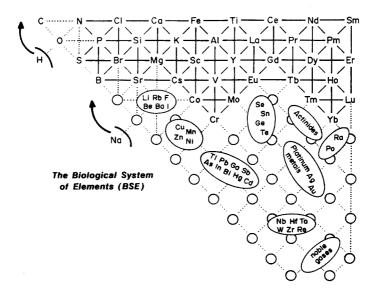


Figure 3 - The Biological System of the Elements (BSE) compiled from data on correlation analysis, physiological function of the individual elements in the living organism, evolutive development out of the inorganic environment and with respect to their uptake form by the plant organism as a neutral molecule or charged ion. The elements H and Na exercise various functions in the biological system so that they are conclusively fixed. The ringed elements can at present only be summarized as groups of elements with a similar physiological function, since there is a lack of correlation data or these data are too imprecise (from MARKERT, 1994 c).

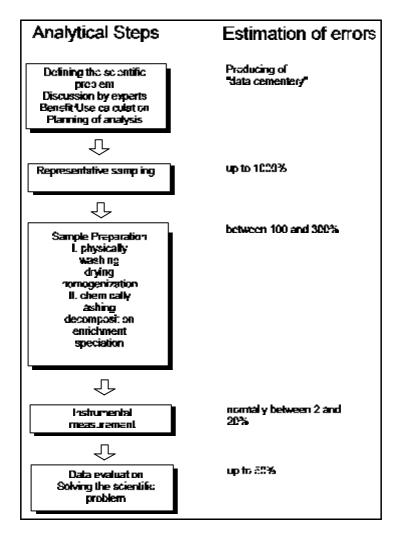


Figure 4 - Simplified analytical flow chart for chemical multielement analysis (from MARKERT, 1993 b). The full flow chart can be found in MARKERT, 1993 a.

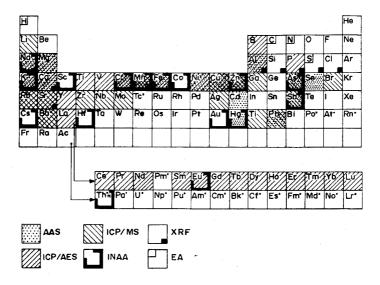


Figure 5 - Matrix-dependent detection sensitivity of different instrumental measuring procedures. Uncontaminated plant material served as the matrix (from MARKERT, 1993 b). Total reflection fluorescence analysis (TRFA) was not included in this overview. However, for quite a number of elements it already achieves detection limits such as those of ICP/MS.

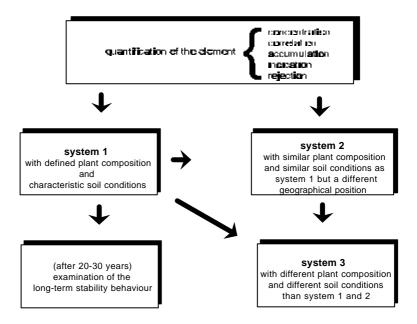


Figure 6 - Comparable aspects of instrumental multielement analysis in ecosystems. Comparability of single system data will be achieved by harmonizing sampling procedure, sample preparation, instrumental measurement and data evaluation (from MARKERT and WTOROWA, 1992).

### PLANNED STRUCTURE OF ECCE

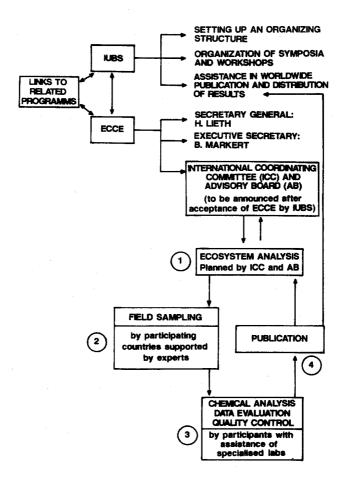


Figure 7 - Structure of the administrative and scientific part of the Element Concentration Cadaster in Ecosystems project (ECCE) supported by the International Union of Biological Sciences (IUBS).

From MARKERT, 1994 a.

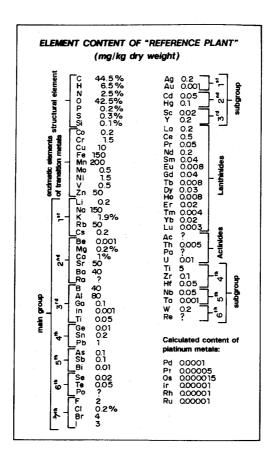


Figure 8 - Data for "reference plant". No data for typical accumulator plants were used. Data were mainly extracted from the analytical work of MARKERT (1993 a). If data for single elements were not available they were collected from BOWEN, 1979 or KABATA PENDIAS and PENDIAS, 1992. The sequence of the elements is based on their position in the chemical periodic table. Exceptions are the biological structural elements C, H, N, O, P and Si and the transition metals Co, Cr, Cu, Fe, Mn, Mo, Ni, V and Zn which have an enzymatic effect (from MARKERT, 1993 a).

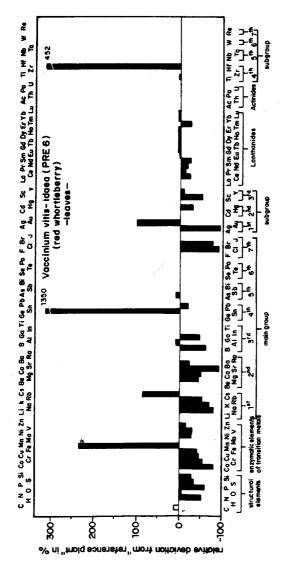


Figure 9 - Chemical fingerprint of Vaccinium vitis-idaea (red whortleberry, leaves) after normalization against "reference plant". The samples were collected in the "Grasmoor" near Osnabrck, Northwest Germany (from MARKERT, 1993 a).

### $(\mu g/I)$ Estimated content of

### **ELEMENT CONTENT OF "REFERENCE FRESHWATER"**

Figure 10 - Data for "reference freshwater". Note: No data for highly polluted water were used. Further explanations are given in Figure 8 (from MARKERT and GELLER, 1994).

Table 1 - Estimation of the total element content in the world plant biomass in t. (From MARKERT, 1992).

·				- 1		- <del></del>	
?	_	Hf	9,2		Ra	?	_
3,682	x10 <sup>5</sup>	Hg	1,841	x10 <sup>5</sup>	Rb	9,2	x10 <sup>7</sup>
1,47		Но	1,472		Re	?	
1,841		I	5,523		Rh	1,84	x10 <sup>1</sup>
1,841	x10 <sup>3</sup>	ln	1,841		Ru	1,84	x10 <sup>1</sup>
7,3640		lr	1,841		S	5,523	x10 <sup>10</sup>
7,3640		K	3,497	x10 <sup>10</sup>	Sb	1,841	x10 <sup>5</sup>
1,841	x10 <sup>3</sup>	La	3,682	x10 <sup>5</sup>	Sc	3,682	x10 <sup>4</sup>
1,841		Li	3,682		Se	3,682	x10 <sup>4</sup>
7,364	x10 <sup>6</sup>	Lu	5,523		Si	1,841	x10 <sup>9</sup>
8,19	x10 <sup>11</sup>	Mg	3,682		Sm	7,364	x10 <sup>4</sup>
1,841	x10 <sup>10</sup>	Mn	3,682		Sn	3,682	x10 <sup>5</sup>
9,2	x10 <sup>4</sup>	Мо	9,2	x10 <sup>5</sup>	Sr	9,2	x10 <sup>7</sup>
9,2	x10 <sup>5</sup>	N	4,602		Ta	1,841	x10 <sup>3</sup>
3,682		Na	2,76		Tb	1,472	x10 <sup>4</sup>
3,682	x10 <sup>5</sup>	Nb	9,2	x10 <sup>4</sup>	Te	9,2	x10 <sup>4</sup>
2,7615	x10 <sup>6</sup>	Nd	3,682	x10 <sup>5</sup>	Th	9,2	x10 <sup>3</sup>
3,682	x10 <sup>5</sup>	Ni	2,76	x10 <sup>6</sup>	TI	9,2	x10 <sup>4</sup>
1,841	x10 <sup>7</sup>	0	7,824	x10 <sup>11</sup>	Ti	9,2	x10 <sup>6</sup>
5,523	x10 <sup>4</sup>	Os	2,7615	x10 <sup>1</sup>	Tm	7,364	x10 <sup>3</sup>
3,682	x10 <sup>4</sup>	Р	3,682	x10 <sup>10</sup>	U	1,841	x10 <sup>4</sup>
1,472	x10 <sup>4</sup>	Pa	?	?	V	9,2	x10 <sup>3</sup>
3,682	x10 <sup>6</sup>	Pb	1,841	x10 <sup>6</sup>	W	3,682	x10 <sup>5</sup>
2,76	x10 <sup>8</sup>	Pd	1,841	x10 <sup>2</sup>	Υ	3,682	x10 <sup>5</sup>
1,841	x10 <sup>5</sup>	Po	?		Yb	3,682	x10 <sup>4</sup>
7,364	x10 <sup>4</sup>	Pr	9,2		Zn	9,2	x10 <sup>7</sup>
1,841	x10 <sup>4</sup>	Pt	9,2	x10 <sup>1</sup>	Zr	1,841	x10 <sup>5</sup>
	1,47 1,841 1,841 7,3640 7,3640 1,841 1,841 7,364 8,19 1,841 9,2 9,2 3,682 2,7615 3,682 2,7615 3,682 1,841 5,523 3,682 1,472 3,682 2,76 1,841 7,364	3,682 x10 <sup>5</sup> 1,47 x10 <sup>8</sup> 1,841 x10 <sup>5</sup> 1,841 x10 <sup>3</sup> 7,3640 x10 <sup>7</sup> 7,3640 x10 <sup>7</sup> 1,841 x10 <sup>3</sup> 1,841 x10 <sup>4</sup> 7,364 x10 <sup>6</sup> 8,19 x10 <sup>11</sup> 1,841 x10 <sup>10</sup> 9,2 x10 <sup>4</sup> 9,2 x10 <sup>5</sup> 3,682 x10 <sup>9</sup> 3,682 x10 <sup>5</sup> 2,7615 x10 <sup>6</sup> 3,682 x10 <sup>5</sup> 1,841 x10 <sup>7</sup> 5,523 x10 <sup>4</sup> 3,682 x10 <sup>5</sup> 1,472 x10 <sup>4</sup> 3,682 x10 <sup>6</sup> 2,76 x10 <sup>8</sup> 1,841 x10 <sup>5</sup> 7,364 x10 <sup>4</sup>	3,682 x10 <sup>5</sup> Hg 1,47 x10 <sup>8</sup> Ho 1,841 x10 <sup>5</sup> I 1,841 x10 <sup>7</sup> Ir 7,3640 x10 <sup>7</sup> K 1,841 x10 <sup>3</sup> La 1,841 x10 <sup>4</sup> Li 7,364 x10 <sup>6</sup> Lu 8,19 x10 <sup>11</sup> Mg 1,841 x10 <sup>10</sup> Mn 9,2 x10 <sup>4</sup> Mo 9,2 x10 <sup>5</sup> N 3,682 x10 <sup>5</sup> N 3,682 x10 <sup>5</sup> Nb 2,7615 x10 <sup>6</sup> Nd 3,682 x10 <sup>5</sup> Ni 1,841 x10 <sup>7</sup> O 5,523 x10 <sup>4</sup> Os 3,682 x10 <sup>4</sup> P 1,472 x10 <sup>4</sup> Pa 3,682 x10 <sup>6</sup> Pb 2,76 x10 <sup>8</sup> Pd 1,841 x10 <sup>5</sup> Po 7,364 x10 <sup>4</sup> Pr	3,682	3,682 x10 <sup>5</sup> Hg 1,841 x10 <sup>5</sup> 1,47 x10 <sup>8</sup> Ho 1,472 x10 <sup>4</sup> 1,841 x10 <sup>5</sup> I 5,523 x10 <sup>6</sup> 1,841 x10 <sup>3</sup> In 1,841 x10 <sup>2</sup> 7,3640 x10 <sup>7</sup> Ir 1,841 x10 <sup>2</sup> 7,3640 x10 <sup>7</sup> K 3,497 x10 <sup>10</sup> 1,841 x10 <sup>3</sup> La 3,682 x10 <sup>5</sup> 1,841 x10 <sup>4</sup> Li 3,682 x10 <sup>5</sup> 1,841 x10 <sup>6</sup> Lu 5,523 x10 <sup>3</sup> 8,19 x10 <sup>11</sup> Mg 3,682 x10 <sup>5</sup> 1,841 x10 <sup>10</sup> Mn 3,682 x10 <sup>5</sup> 1,841 x10 <sup>10</sup> Mn 3,682 x10 <sup>8</sup> 9,2 x10 <sup>4</sup> Mo 9,2 x10 <sup>5</sup> 9,2 x10 <sup>5</sup> N 4,602 x10 <sup>10</sup> 3,682 x10 <sup>5</sup> N 4,602 x10 <sup>10</sup> 3,682 x10 <sup>5</sup> Nb 9,2 x10 <sup>4</sup> 2,7615 x10 <sup>6</sup> Nd 3,682 x10 <sup>5</sup> 3,682 x10 <sup>5</sup> Ni 2,76 x10 <sup>6</sup> 1,841 x10 <sup>7</sup> O 7,824 x10 <sup>11</sup> 5,523 x10 <sup>4</sup> Os 2,7615 x10 <sup>1</sup> 3,682 x10 <sup>4</sup> P 3,682 x10 <sup>10</sup> 1,472 x10 <sup>4</sup> Pa ? ? 3,682 x10 <sup>6</sup> Pb 1,841 x10 <sup>6</sup> 2,76 x10 <sup>8</sup> Pd 1,841 x10 <sup>6</sup> 2,76 x10 <sup>8</sup> Pd 1,841 x10 <sup>2</sup> 1,841 x10 <sup>5</sup> Po ? 7,364 x10 <sup>4</sup> Pr 9,2 x10 <sup>4</sup>	3,682         x10 <sup>5</sup> Hg         1,841         x10 <sup>5</sup> Rb           1,47         x10 <sup>8</sup> Ho         1,472         x10 <sup>4</sup> Re           1,841         x10 <sup>5</sup> I         5,523         x10 <sup>6</sup> Rh           1,841         x10 <sup>3</sup> In         1,841         x10 <sup>3</sup> Ru           7,3640         x10 <sup>7</sup> K         3,497         x10 <sup>10</sup> Sb           1,841         x10 <sup>3</sup> La         3,682         x10 <sup>5</sup> Sc           1,841         x10 <sup>4</sup> Li         3,682         x10 <sup>5</sup> Se           7,364         x10 <sup>6</sup> Lu         5,523         x10 <sup>3</sup> Si           8,19         x10 <sup>11</sup> Mg         3,682         x10 <sup>5</sup> Sm           1,841         x10 <sup>10</sup> Mn         3,682         x10 <sup>5</sup> Sr           9,2         x10 <sup>4</sup> Mo         9,2         x10 <sup>5</sup> Sr           9,2         x10 <sup>5</sup> N         4,602         x10 <sup>10</sup> Ta           3,682         x10 <sup>5</sup> Nb         9,2         x10 <sup>5</sup> Th           3,682         x10 <sup>5</sup>	3,682         x105         Hg         1,841         x105         Rb         9,2           1,47         x108         Ho         1,472         x104         Re         ?           1,841         x105         I         5,523         x106         Rh         1,84           1,841         x103         In         1,841         x103         Ru         1,84           7,3640         x107         K         3,497         x1010         Sb         1,841           1,841         x103         La         3,682         x105         Sc         3,682           1,841         x104         Li         3,682         x105         Se         3,682           1,841         x106         Lu         5,523         x103         Si         1,841           8,19         x1011         Mg         3,682         x105         Sm         7,364           1,841         x1010         Mn         3,682         x108         Sn         3,682           9,2         x104         Mo         9,2         x105         Sr         9,2           9,2         x105         N         4,602         x1010         Ta         1,841 </td

Table 2 - Element content of plants investigated in the Kalinin area in comparison with similar plant species taken in a forest ecosystem in Germany ("Grasmoor" near Osnabrck).

Data are given, unless otherwise specified, in mg/kg dry weight. From MARKERT and WTOROWA, 1992). VACVIT: Vaccinium vitis-idaea; VACMYR: Vaccinium myrtillus; POLCOM: Polytrichum commune; POLFOR: Polytrichum formosum; SPHSPE: different Sphagnum species; HYPPHY: Hypogymnum physodes; PICABI: Picea abies; PINSYL: Pinus sylvestris.

	VA	CVIT	VAC	MYR	POLCOM	POLFOR	SPI	ISPE	НҮРРНҮ	PICABI	PINSYL
	USSR	FRG	USSR	FRG	USSR	FRG	USSR	FRG	USSR	USSR	FRG
Ac Ag Al As Au	130.4 0.5	- 87 0.108	273.6 0.090	0.14 158 0.22	305 0.095	0.302 306 0.198	214.6 0.965	0,3 482 0.23	- - 638 1.31	99.5 0.090 0.0026	0.174 142 0.214 0.004
B Ba Be Bi Br	34,8	14 31 - - 0.91	60	21 29 - - 3.61	7.8 - - 2.5	0.2 4.5 - - 3.16	- 10 - - - 2.27	0.2 5.4 - - 6.09	- 23 - - 11.5	- 15 - - 1.54	20 1.1 - - 2.91
C Ca Cd Ce CI	51.7% 3240 0.085 011	50.2% 4900 - 0.39 100	45.9%9 9900 0.185 0.217	47.8% 6500 - 0.29 1530	44.7% 2710 0.205 0.26	44.8% 1000 - 0.51 670	43.6% 194 0.31 0.442	42.6% 550 - 141 670	46% 810 0.245 1.865	50.1% 6100 0.32 0.208	51.4% 1200  031 431
Co Cr Cs Cu Dy	0.185 2.0 0.147 9.07 0.008	0.037 051 0.371 5.5 0.030	0.083 - 0.215 6.14 0.014	*0.06 0.95 0.317 4.9 0.026	0.289 1 0.36 16.48 0.017	0.300 3.67 0.33 12.7 0.041	0.244 0.72 0.218 21 0.042	0.8 6.4 0.74 6.65 0.099	0.355 2.23 0.185 10.9 0.10	0.083 0.73 0.099 4.0 0.011	0.124 1.72 0.098 4.28 0.024
Er Eu F Fe Ga	0.005 0.002 - 91.8 0.31	0.020 0.008 - 82 0.054	0.008 0.006 - 111.4 0.11	0.017 0.007 - 130 0.14	0.010 0.0085 - 165	0.028 0.008 184 0.14	0.042 0.025 0.010 207 0.42	0.066 0.013 - 364 0.12	0.10 0.062 0.030 - 664 0.405	0.011 0.007 0.007 - 79.32 0.42	0.024 0.016 0.006 - 118 0.117
Gd Ge H Hf Hg	0.010 - 6,6 -	0.04 - 6.5% 0.276 0.072	0.016 5.84%	0.034 6.02% 0.415 0.067	0.020 - 5.99% - -	0.054 - 6.05% 0.079 0.28	0.050 5.95%	0.13 5.91% 0.631 0.417	0.12 6.27% 0.165% 0.260	0.014 6.12%	0.032 - 6.77% 0.058 0.0995
Ho In K La	0.002 - - 7966 0.057	0.008 - - 5850 0.2	0.002 - - 8280 0.16	0.007 - - 7000 0.15	0.003 - - 15390 0.24	0.011 - - 9000 0.26	0.008 - - 11.470 0.265	0.025 - - 9100 0.72	0.020 - - 3655 0.91	0.002 - - 5600 0.194	0.006 - 4400 0.16

Table 2 - Element content of plants investigated in the Kalinin area in comparison with similar plant species taken in a forest ecosystem in Germany ("Grasmoor" near Osnabrck).

Data are given, unless otherwise specified, in mg/kg dry weight. From MARKERT and WTOROWA, 1992). VACVIT: Vaccinium vitis-idaea; VACMYR: Vaccinium myrtillus; POLCOM: Polytrichum commune; POLFOR: Polytrichum formosum; SPHSPE: different Sphagnum species; HYPPHY: Hypogymnum physodes; PICABI: Picea abies; PINSYL:Pinus sylvestris. (continuous)

	VACVIT		VACMYR		POLCOM	POLFOR	SPHSPE		НҮРРНҮ	PICABI	PINSYL
	USSR	FRG	USSR	FRG	USSR	FRG	USSR	FRG	USSR	USSR	FRG
Li	-	0.003	0.2	0.2	•	0.37	0.28	0.4	0.885	0.29	0.475
Lu	0,008	1100	0.001	0.003	0.001	0.004	0.004	0.01	0.01	0.001	0.003
Mg	1590	674	4047	1600	240	439	696	452	293	650	733
Mn	1200	-	3981	604	179	30	272	22	149	718.5	208
Mo	0.425		0.4	0.4	0.2	1.6	0.5	2.34	0.4	0.24	0.62
N	1.48%	1.15%	2.29%	2.15%	1.84%	1.65%	1.39%	1.72%	1.13%	1.0%	2.24%
Na	272	29	440	50	60.4	, 180	427	430	129	425	101
Nb	0.085	-	0.065	0.021	0.07	0.037	0.07	0.031	0.08	0.08	0.0275
Nd	0.044	0.17	0.088	0.12	0.095	0.22	0.02	0.6	0.58	0.074	0.13
Ni	4.0	1.1	2.2	-	1.34	0.6	3.48	1.7	3.405	3.95	1.4
0	-	40%	-	41.4%	-	45.5%	-	46.9%	-	١ ٠	37.4%
P	1 - 1	746	١.	1090	i -	1200	-	916	1 -	١ -	950
Рa				-	-	] -	-	-	-	· -	l :
Pb	5.75	0.8	3.005	2.25	2.675	0.35	459	7.25	8.59	4.075	4.75
Po	-	-	١ -	-		-	-	<u> </u>	<u> </u>	-	<u> </u>
Pr	0.014	0.044	0.026	0.033	0.029	0.058	0.061	0.1	0.18	0.023	0.035
Ra	-		١.	-	-	-	-	-	-	ļ -	
Rb	17.0	22.5	26.3	30	37	23	29.25	45	7.37	18	8.1
Re	-	-	-	٠ ا	-	-	-		-	-	1
S	1000	2000	2300	3140	800	2100	300	1940	1300	<u> </u>	2200
Sb	<del>                                     </del>	T -	-	0.071	-	0.16	0.053	0.11	0.265	l	0.084
Sc	0.0046	0.009	0.0125	0.015	02279	0.025	0.0377	0.036	0.196	0.0173	0.015
Se	-	١.	l -	١.	1 -	i -	l -	-	0.39	l -	l .:.
Si	١.	700	-	670	-	1390		1120		l	966
Sm	0.009	0.030	0.018	0.020	0.018	0.039	0.040	0.11	011	0.015	0.021
Sn	1 -		-	0.002	0.061	0.037	0.066	0.016	0.193	0.028	0.004
Sr	-	-	١.	١.	-	-	0.01	-	-	0.01	l
Ta	١.	5.1	١.	4.7		6.4	-	9.5	<b>-</b> .	1	5.1
Tb	0.001	0.003	0.002	0.003	0.002	0.005	0.005	0.011	0.012	0.002	0.006
Te	0.045	-				-	0.11	<u> </u>	<u> </u>	0.11	<u> </u>
Th		-	T -	0.002	0.061	0.037	0.066	0.016	0.193	0.028	0.004
TI		i -	-	-	-	-	0.01		-	0.01	l
ΤÏ		5.1	-	4.7	-	6.4	-	9.5	1	1	5.1
Tm	0.001	0.003	0.002	0.003	0.002	0.005	0.005	0.011	0.012	0.002	0.006
U	0.045		<u> </u>	<u> </u>	<u> </u>	<u> </u>	0.11	<u> </u>		0.11	
	0.08	0.33	0.13	-	0.37	0.574	0.16	1.2	1.5	0.16	0.65
W	2.6	١.	0.44	-	0.22	l -	0.065		1	0.2	1
Υ	0.046	0.18	0.076	0.16	0.091	0.25	0.23	0.59	0.58	0.064	0.15
Yb	0.005	0.02	0.008	0.017	0.010	0.027	0.024	0.065	0.062	0.007	0.016
Zn	28.6	42	13.87	20	46.45	58	36.25	36	72	29.65	53
Zr	0.045	T -	0.07	0.13	0.125	0.21	0.2	-	0.525	0.07	0.13

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