Biogeochemical studies — the present state of knowledge

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Biogeochemia jest jedną z najbardziej dynamicznie rozwijających się dyscyplin nauk o Ziemi. Pobudza ona rozwój metod geoanalitycznych i otwiera nowe perspektywy dla interpretacji wyników badań. W artykule omówiono podstawowe pojęcia z zakresu biogeochemii, podano też przykłady zastosowań badań biogeochemicznych w geologii i ochronie środowiska. Do najbardziej spektakularnych należą odkrycia wielu złóż polimetalicznych w USA i Kanadzie oraz wytyczanie przebiegu uskoków (Chaffee, 1975; Dunn i in., 1992). Istotnym elementem badań biogeochemicznych są rośliny. Znalazły one zastosowanie w biomonitoringu skażeń atmosferycznych. Do klasycznych należą badania bioindykacyjne, prowadzone przy użyciu porostów, mchów i drzew szpilkowych. Oznaczenia składu chemicznego i izotopowego (głównie siarki) w wymienionych biowskaźnikach służą do identyfikacji źródeł skażeń (Case & Krouse, 1980; Crock i in., 1992a, b, 1993; Jackson i in., 1996).

Skład chemiczny roślin zależy od wielu czynników topograficznych, klimatycznych, edaficznych, fizjologicznych i genetycznych (Kabata-Pendias & Pendias, 1992; Migaszewski, 1998a; Migaszewski & Gałuszka, 1998). Stwarza to duże trudności w interpretacji wyników analiz chemicznych roślin (tab. 1–3), jak również zmusza do ścisłego przestrzegania warunków opróbowania, szczególnie w przypadku badań regionalnych.

Badania biogeochemiczne powinny stanowić integralną część projektów geochemicznych. Należy je stosować przy rejestracji koncentracji pierwiastków śladowych w bioindykatorach roślinnych na obszarach ścisłej ochrony (Migaszewski i in., 1998), a także w rejonach skażeń antropogenicznych (Migaszewski & Pasławski, 1996; Migaszewski i in., 1998; Migaszewski, 1998a–c). Rośliny wykorzystuje się również w rekultywacji biologicznej terenów górniczych lub obszarów skażonych (Migaszewski & Gałuszka, 1998). Znajdują one zastosowanie w badaniach nad wpływem wód kopalnianych na różne systemy biotyczne (King, 1995). Rośliny należące do tzw. „akumulatorów" są wykorzystywane jako źródło niektórych metali (Dunn i in., 1992).

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Biogeochemistry is one of the most dynamically developing discipline of geosciences. It stimulates geoanalytical methods and opens new perspectives for interpretation. Its practical aspects encompass not only environmental protection, but also geology, mining, agriculture, medicine, etc. As an interdisciplinary science, biogeochemistry implies a close cooperation of geochemists, geologists, chemists, biologists, soil and forest scientists, geophysicists, isotope physicists, etc.

This report is a brief summary of many articles by the present authors regarding geochemistry of soils and rocks, and biogeochemistry of plant indicators published in *Przegląd Geologiczny, Geological Quarterly* and *Water, Air, and Soil Pollution.* It also includes relevant data contained in on-file reports of the Polish Geological Institute and the US Geological Survey (see references in Migaszewski et al., 1998). Numerous examples have been taken especially from western parts of the USA, Canada and the Holy Cross Mts, Poland.

Biogeochemical and geochemical investigations use basically the same geoanalytical methods. The mentioned last have been outlined in this issue's article (Migaszewski et al., 1998) and in Migaszewski (1998 a–c).

Basic notions of biogeochemistry

Biogeochemistry is a branch of geochemistry dealing with the migration and spatial distribution of chemical elements in plants, animals and man making up the biosphere — an integral part of lithosphere, pedosphere, atmosphere and hydrosphere. Living organisms trigger the flow of matter, energy and „information" in-between ecosystems, thus influencing the chemical composition of the Earth's outermost layers. Sparked by the sun (or photochemical) energy, the living matter forms from the inorganic one, then decays passing into mineral substance. A large group of sedimentary rocks and mineral deposits is of organic origin.

All living organisms need chemical elements for survival. They are labeled as **bioessential**. Some of them occur in traces (generally less than 1%). The bioessential elements to all plants, animals and man include C, Ca, H, K, Mg, N, Na, O, P, S, and in traces Cl, Cu, Fe, Mn, Se, Zn (Gough, 1993). Many elements are bioessential only to one or a few species, or several classes of plants and animals. **Contaminants** are elements or substances that occur above background levels. Those contaminants potentially detrimental to organisms are termed **hazards (toxicants)**. The gap between bioessential and toxic concentrations of these elements is sometimes very narrow; tolerance limits of selenium in plants for cattle and sheep range from 0.4 to 4 $\mu g\ g^{-1}$ or ppm (dry weight) (Lakin & Davidson, 1975). A dose over 4 $\mu g\ g^{-1}$ Se is toxic to animals. Subacute poisoning associated with damage to the central nervous system, known locally as blind staggers, loco disease or pushing disease, has been reported in the western United States, and South Africa (Gough et al., 1979). In turn, deficiency of this element leads to chronic diseases including muscle deformations, liver and pancreas tissue necrosis, drop in fertility, improper development of teeth, hair or feathers (Kabata-Pendias & Pendias, 1979). Selenium is not toxic to plants (Herring, 1990). Such elements as As, Be, Cd, Cr, Hg, Pb, not required (if so, only in the range of ppb or ppt) by plants, animals and man are considered **non-bioessential**.

To determine whether a plant, an animal, a man, a soil, a sediment or a rock contains high or low concentrations of a given chemical element or an organic compound, it is important to know what concentration is normal (natural). The first measurement is termed a **baseline** and the other a **background**. Baseline concentrations usually expressed as a range, represent a measurement of a given sample in a specific location and time. They vary in areas of different pollution. Baseline studies can assess chemical pattern changes in the environment resulted from man's activity. In pristine areas, baseline concentrations are close to background ones. The term mentioned last implies concentrations of chemical elements or organics recorded in plants, soils, and sediments before the man's industrial activity started. Such samples that have a minimum human impact have been derived from herbaria, tree rings, glacial ice, or sea and lake sediment cores, etc.

In general, an increased amount of an element in bedrock leads to a higher concentration of it in vegetation. However, each species has its own specific requirements and tolerance to different elements, or more precisely to their specific soluble forms. The ability of such a chemical form to be incorporated into plant and animal tissue is labeled as **bioavailability** (Gough, 1993). The pH and redox potential of soils are generally basic parameters that control solubility and speciation of elements in the environment. This phenomenon is well exemplified by selenium. Soils containing more than 10 $\mu g\ g^{-1}$ Se can produce toxic levels in plants, for example in South Dakota and Kansas, but the soils from humid areas of Hawaii and Puerto Rico, containing up to 26 $\mu g\ g^{-1}$ Se, support nontoxic vegetation. In the latter two areas the soils are acidic and contain an abundance of iron. Acidic soils seem to favor the more reduced, complexed forms of this element (iron selenites), which are not readily available to plants. In turn, oxidation by chemical and bacterial processes in alkaline soils favors the formation of selenates, which are readily absorbed by plants (Mayland, 1985, cited from Herring, 1991).

Plants react to the excess of harmful elements by redistributing them in their organs. The most harmful are accumulated in the outermost parts of trees or bushes, i.e., in outer bark, twigs and tops. In some measure, this phenomenon resembles the human body where non-bioessential elements, such as arsenic and lead, are pushed to its extremities (hair, fingernails). This way, different anatomic and morphologic parts of plants show diverse chemical composition (tab. 1). Thinner twigs reveal a higher level of elements than thicker twigs. Biogeochemical studies also showed that the 2–6 year black spruce *Picea mariana* (Miller) BSP twig growth contained much more uranium than the older growth (Dunn et al., 1992). If a tree is exposed to heavy atmospheric pollution, the best part reflecting natural (geologic) concentrations is trunkwood. On the other hand, this part of tree shows a very low ash yield (less than 0.5%), so during ashing metals are concentrated up to 400-folds.

Tab. 1. Distribution pattern of gold ($\mu g\ kg^{-1}$ in dry tissue) within sagebrush *Artemisia tridentata* Nutt. (Smith & Kretchmer from Dunn et al., 1992)

Plant parts	Au (in $\mu g\ kg^{-1}$)
Buds	1.92
Leaves	0.85
Twigs	0.61
Large twigs	0.39
Branches	0.80
Trunk	1.76
Upper roots	1.39
Roots	0.91

Based on the diverse uptake of elements by plants, Kovalevskii (1976) proposed the so-called „**barrier concept**". The „**barrier plants**" absorb elements only to some levels needed for growing. If elements occur in excess in soil or rock, they are not taken up by roots of these plants, but if so, they are accumulated either in inert tissues or in a cellular membrane or various organelles of active cells. Plant roots tend to pass through a toxic soil zone and absorb elements from uncontaminated portions of a soil profile. Some elements are sometimes removed from the plants, for instance, in the form of H_2S (Case & Krouse, 1980; Migaszewski & Pasławski, 1996; Migaszewski & Gałuszka, 1997) or volatile Hg-, Pb-, Se- and Sn-organic compounds (Herring, 1991; cited from Kabata-Pendias & Pendias, 1992). The „**non-barrier**" plants absorb elements in a consistent plant-soil/rock ratio regardless of their levels in soil and rock, for instance, *Viola calaminaria* can take up several percent of zinc (cited from Polański & Smulikowski, 1969), whereas legumines of the genus *Astrogalus* can contain even 1% Se (Emerick & DeMarco, 1991).

Biogeochemical studies for geology and the environment

Living organisms are greatly influenced by the chemical composition of the Earth's outer layers and reflect any geochemical anomalies or changes that take place there. In fact, any plant or animal species and even man can be a bioindicator. Nonetheless, only plants can directly reflect geochemistry of soils and/or rocks they grow in, or monitor air pollution. The significance of plant bioindicators also results from the fact that they occupy stationary position compared to animals and man; besides, they can be examined and sampled periodically using same methods.

Of different taxonomic groups, lichens, mosses and conifers are commonly applied for biomonitoring of air quality. Lichens, the most important of all bioindicators, have been studied since the 19th century along with the development of heavy industry in Europe (Nylander, 1866, 1896 — cited from Richardson, 1991) and North America. Lichen thalii, moss tissues, and conifer bark and needles can record concentration baselines of elements and organics, as well as variations in sulfur and lead isotope composition. The results obtained indicate the degree and extent of environmental pollution (Grodzińska, 1971, 1980; Case & Krouse, 1980; Richardson, 1991; Crock et al., 1992a, b, 1993; USDA ..., 1993; Migaszewski, 1996; Migaszewski & Gałuszka, 1997, and references cited therein). A good bioindicator of trace metals is dandelion that can monitor air/soil pollution (Kabata-Pendias & Dudka, 1991). Elemental or isotopic „fingerprints" of plants are commonly used for identifying industrial pollution sources (Crock et al., 1992a, b, 1993; Jackson et al., 1996).

Many anatomic and morphologic parts of vascular plants reflect primarily the chemical composition of their bedrock; this phenomenon has been applied in prospecting for ore mineral deposits, as well as for tracing fault patterns. This kind of investigations involves geobotany and biogeochemistry (Cannon, 1957; Brooks, 1979; King et al., 1984; Kovalevskii, 1987; Dunn et al., 1992). The first observations made by Vitruvius in 1 century B.C. gave a rise to these studies (Viktorov, 1961).

Some visible features including stunted growth, gigantism, odd shapes and colors resulting from abundance or deficiency of some elements have been used in geobotanical studies. They have successfully been applied in arid and semiarid areas. Some large copper, gold and uranium deposits were discovered as a result of these studies (Cannon, 1957, Erdman et al., 1988). They included many porphyry copper deposits of the southwest United States (Chaffee, 1975).

Under moderate and boreal climatic conditions plants do not show any visual changes resulted from natural (geologic) anomalies provided they are not affected by excessive emissions of atmospheric pollutants. The mentioned last lead to visual injuries (chlorosis and necrosis) of conifer needles and devastated changes in forest ecosystems (Freemantle, 1995). In unpolluted areas, for instance, in some parts of Canada, sophisticated chemical techniques have been used in the search for metal anomalies in different plant organs. The world class Athabasca uranium deposit in Canada was discovered owing to anomalous concentrations of this element (5–886 $\mu g\ g^{-1}$) in black spruce [*Picea mariana* (Miller) BSP] twigs. The Bf soil horizon underlying each tree did not show an increased level of uranium (1.8–2.5 $\mu g\ g^{-1}$) (Dunn et al., 1992).

An impact of natural (geologic) toxic substances on different environmental systems, especially biota, is a concern. Ore mineral, coal, crude oil and natural gas deposits or mineralized rock formations are a potential source of pollution. Extraction of these raw materials provides many toxic elements, such as As, Be, Cd, Cr, Hg, Pb, U, for the environment, especially for streams, groundwaters, soils and vegetation (Gough et al., 1979; Manahan, 1994). Acid mine drainage poses environmental problems in the Rockies (USA), where numerous abandoned mine workings are located (Stewart & Severson, 1994; King, 1995).

Plants can also be used for biological reclamation of mine soils and overburden (Williams & Schuman, 1987), as well as for remediation of polluted areas. The biomass of some non-barrier plants containing trace metals can be incinerated. This way some useful elements can be extracted.

Interpretative traps of plant geochemistry and their impact on sampling

Interpretation of plant geochemistry is far more complex than soil and rock geochemistry. The chemical composition of plants depends on many natural factors, i.e., topographic (elevation, extent of mountain ranges), climatic (insolation, wind, temperature, moisture), edaphic (structural and physico-chemical properties of soil), physiologic and genetic. Local topographic, climatic and edaphic variables are generally linked to the geologic setting of a given area.

This fact gives a potential challenge to data interpretation. The example of it is the production of metal chelating acids (especially usnic acid and atranorin) in larger amounts by lichens as elevation increases — causing metal concentrations in lichens at higher elevations to be higher (Greene, 1993). The angle of the slope and its aspect control the evapo-transpiration processes which in the northern hemisphere is more intense on south facing slopes. In the moderate climatic zone, northern slopes keep more moisture (snow lies longer there), but on the other hand, they are shorter exposed to the sun.

Seasonal variations in plant geochemistry influence metabolic processes. In spring, at the peak of vegetative growth, plants show higher assimilation of many nutrients including trace elements (tab. 2). Annual variations also play an important role in the chemical composition of plants, except for dead tissues, for instance, outer bark. In both cases the element uptake depends on the plant phenology (influence

Tab. 2 . Seasonal variations in the content of gold ($\mu g\ kg^{-1}$ in ash) in alder (*Alnus*) twigs (Dunn et al., 1992)

Site	Au (in $\mu g\ kg^{-1}$)			
	1984			1985
	Early June	Early August	Mid September	Mid Aprill
1	32	7	23	250
2	53	6	17	47
3	58	9	20	130
4	34	6	15	166
5	29	8	10	37
6	35	7	11	34
7	23	6	13	57
8	25	8	13	41
9	25	11	20	27
10	8	20	14	20

of climate). During dry seasons, metabolism and absorption of elements are retarded. Each plant species reacts differently to daily, seasonal and annual climatic fluctuations.

The structure of soil, the pH, the redox potential, the content and type of clay minerals (montmorillonites and zeolites of high cation exchange capacity vs illites and kaolinites featured by lesser ionic sorption), organic matter, and other sorbents (phosphates, oxides and hydrooxides), as well as the concentration of microflora, micro- and mesofauna, have an impact on the geochemistry of plants.

Each plant takes up different chemical forms. The type and form (soluble or insoluble) of minerals occurring in soils, rocks or airborn particulates are important when some elements are hazardous to the environment, for instance, neutral insoluble chromite $[Cr^{3+}{}_2O_3]$ resistant to weathering versus potentially toxic soluble chromates $[(Cr^{6+}O_4)^{2-}]$. If two or more toxic elements are present, they reveal synergistic (much stronger), antagonistic (much weaker) or additive (stronger) effects. In the case mentioned last, an inactive element or substance enhances the action of an active toxicant.

Aside from the physiologic factors, the genetic ones are highly unpredictable. The studies showed that very young and old species are especially succeptible to toxic substances. Some individuals within a given population of species are extremely sensitive or exceptionally resistant to toxicants (Manahan, 1994).

Considering this, some precautions must be taken while collecting plant samples, especially for regional studies. In each case the rule BE CONSISTENT should always be observed. These basic rules are as follows:

(i) Collect same plant species or their morphologic/anatomic parts. The best examples are bioindicators of air quality largely spread in Europe. They include the lichen species *Hypogymnia physodes* (L.) Nyl., Scots pine *Pinus sylvestris* L. or the moss species *Hylocomium splendens* Hedw. The species mentioned last shows the largest extent (found even in Alaska) and can be used for global comparisons. It should be emphasized here that lichens, they should be taken from the same tree bark due to the diverse biogeochemistry of the same lichen species (tab. 3).

(ii) Collect samples of similar age and appearance, for instance, same lichen species from the same tree bark, and tree height and diameter, from sites featured by similar elevation above sea level, aspect and habitat, as well as at a distance from traffic roads.

(iii) Collect samples in the same season (in the northern temperate climatic zone in June through July) within a 2–3 week period of time.

(iv) Don't smoke, don't wear any gold, silver or copper jewelry and (if possible) use surgical gloves.

(v) Avoid any outside contamination of samples, for instance, use steel tools and proper bags, don't use plastic shovels or scrapers for organics determinations, keep bags with soils, rocks and vegetation separately.

(vi) Dry or (if possible, freeze-dry) samples at an ambient temperature on the same day; this way any changes in elemental and isotopic composition due to the growth of molds and fungi will be avoided.

Conclusions — what should be done?

An increasing impact of pollution on biota and ecosystems in a broader sense has become a real concern. No matter how complex natural and anthropogenic causes are, they always affect the biosphere. This is the main reason why biogeochemistry will be playing a greater role in the future environmental studies. International and interdisciplinary projects need to employ same sampling and geoanalytical methods. Chemical analyses ought to be performed primarily on tissues not ashes. Chemical speciation (sequential) techniques should be developed to assess the mobility, bioavailability and potential toxicity of such elements as As, Be, Cd, Cr, Hg, Pb, Se, etc. (Chłopecka et al., 1996). It will help assess the toxicity of elements to organisms. The biogeochemical investigations need to be carried out on the

Tab. 3. Concentrations of selected elements and variations in stable sulfur isotopes in the lichen thalii *Hypogymnia physodes* (L.) Nyl. from deciduous vs coniferous trees (Migaszewski, 1996)

Sample Symbol	Ba $\mu g\ g^{-1}$	Ca %	Cd $\mu g\ g^{-1}$	Cu $\mu g\ g^{-1}$	Fe %	Hg $\mu g\ g^{-1}$	K %	Mn $\mu g\ g^{-1}$	P %	Pb $\mu g\ g^{-1}$	S %	$\delta^{34}S$ ‰	Sr $\mu g\ g^{-1}$	Zn $\mu g\ g^{-1}$
C-birch	40	0.19	0.8	7	0.08	0.17	0.30	144	0.179	25	0.080	3.4	5	71
C-pine	18	0.08	1.0	7	0.09	–	0.22	53	–	16	–	4.5	3	170
F/1-birch	13	0.49	0.8	6	0.05	0.13	0.30	108	0.087	33	0.058	4.7	5	138
F/1-pine	8	0.15	0.9	8	0.09	0.17	0.23	38	0.067	14	0.094	4.8	3	98
I-oak	55	0.51	0.6	10	0.10	0.23	0.33	230	0.129	23	0.095	4.7	4	93
I-pine	10	0.10	0.9	8	0.10	0.24	0.24	51	0.083	18	0.097	4.9	3	100
II-oak	92	2.24	1.3	11	0.06	0.19	0.25	525	0.092	16	0.094	3.2	12	66
II-pine	11	0.25	1.1	10	0.09	0.21	0.26	76	0.080	18	0.098	5.0	4	108
IV-rowan	43	1.22	1.1	11	0.15	0.27	0.23	95	0.078	99	0.092	3.9	13	133
IV-spruce	25	0.20	0.9	12	0.23	0.33	0.20	66	0.085	39	0.119	4.2	5	113
VII-rowan	59	0.66	0.7	11	0.25	–	0.23	97	0.083	83	0.112	4.6	9	145
VII-spruce	30	0.11	0.9	13	0.26	0.27	0.19	44	0.079	48	0.128	4.8	4	120

most vastly spread plant species in order to make global environmental comparisons.

Due to their great significance, biogeochemical programs should be incorporated into the national environmental strategy. Its principal objectives would include:

(i) Monitoring of air quality with plant bioindicators (Migaszewski, 1996; Migaszewski & Pasławski, 1996; Migaszewski & Gałuszka, 1997). These studies coupled with phytosociologic survey, as well as soil, sediment, bedrock and stream water investigations should be carried out around the national environmental monitoring network stations every 5 years.

(ii) Biogeoprospecting for ore mineral deposits, as well as for pinpointing potentially toxic metalliferous rock formations, and fault patterns (Chaffee, 1975; Dunn et al., 1992).

(iii) Biogeochemical maps of polluted (urban-industrial) and pristine areas. Of particular significance are biosphere preserves which are gene pools of unique flora and fauna species; besides, they can be used as reference areas for comparative biogeochemical investigations. One of the first attempts at it was geochemical and biogeochemical studies performed in Everglades Nat'l Park of Florida (Jackson et al., 1995).

(iv) Measurements of elemental and organics levels in different natural ecosystems using „barbell" cluster and ANOVA design (Migaszewski & Pasławski, 1996; Migaszewski et al., 1996, 1998; Migaszewski, 1998a-c).

(v) Localization of biogeochemical and geochemical hazardous anomalies on a regional scale. Additional maps could be produced showing relationships between the content of bioavailable forms of toxicants in soils and the degradation effects or diseases in plants, animals and man.

(vi) Acid mine drainage and its influence on different biotic systems (King, 1995).

(vii) Identification of single natural and anthropogenic pollution sources. The latter can be pinpointed using elemental and isotopic spectra, as well as mineral composition of particulates, both in plants and stack ashes, fuel or feedstock derived from industrial facilities (Case & Krouse, 1980; Crock et al., 1992a, b, 1993; Jackson et al., 1996).

(viii) Biologic reclamation of mine soils and overburden, as well as remediation (detoxication) of polluted areas (Migaszewski & Gałuszka, 1998).

(ix) Use of non-barrier plants as a source of metals (Dunn et al., 1992).

(x) Basic studies of rock-soil-plant-atmosphere systems, including water-soil and water-plant interactions, within similar rock and soil profiles in differently polluted areas. The results obtained could explain what concentrations are natural and what are anthropogenic (Kabata-Pendias & Pendias, 1992).

The man's principal task should focus on reducing pollution of the Earth. Toxicants affect not only particular organs or cellular parts, but also influence reproduction systems and genetic code. The growth and the very existence of man is closely connected with the presence of a full spectrum of plant and animal species.

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