

Geochemistry in environmental studies

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W artykule przedstawiono cele i zakres badań geochemicznych na potrzeby środowiska przyrodniczego. Omówiono również w zarysie główne procesy geochemiczne decydujące o obiegu i rozkładzie pierwiastków chemicznych w najbardziej zewnętrznych warstwach Ziemi. Podstawowe znaczenie w badaniach geochemicznych ma wybór odpowiedniej techniki analitycznej. Obecnie do najnowocześniejszych metod zalicza się atomową spektrometrię emisyjną z indukcyjnie sprzężoną plazmą (ICP-AES) lub spektrometrię masową z indukcyjnie sprzężoną plazmą (ICP-MS), atomową spektrometrię absorpcyjną (FAAS), fluorescencję rentgenowską (XRF) i aktywację neutronową (INAA). Zakres oznaczeń i granice wykrywalności pierwiastków chemicznych w skałach, glebach, osadach, roślinności i wodach uzyskiwane w Centralnym Laboratorium Chemicznym Państwowego Instytutu Geologicznego w Warszawie przedstawiono w tabelach 1 i 2. Podano również przykłady najważniejszych projektów geochemicznych i biogeochemicznych realizowanych w Państwowym Instytucie Geologicznym. Obejmują one atlasy geochemiczne gleb, osadów rzecznych, jeziornych i morskich, wód powierzchniowych i podziemnych oraz atlasy radiologiczne, jak również badania podstawowe w zakresie przemieszczania się pierwiastków chemicznych w systemach skały–gleby–rośliny. Projekty geochemiczne i biogeochemiczne powinny stanowić ważny element strategii działania Ministerstwa Ochrony Środowiska, Zasobów Naturalnych i Leśnictwa. Do głównych jej zadań należałyby:

1. Założenie narodowego banku danych geochemicznych i biogeochemicznych, obejmujących analizy chemiczne gleb, osadów rzecznych, jeziornych i morskich, skał, wód powierzchniowych i podziemnych oraz częściowo bioindykatorów roślinnych w relacji do różnych parametrów topograficznych, hydrologicznych, biologicznych, klimatycznych i zagospodarowania przestrzennego. Wymieniony bank powinien stanowić element światowego banku danych (Darnley i in., 1995).
2. Wypracowanie jednolitej metodyki badań w zakresie pobierania i przygotowania próbek oraz technik analitycznych według norm międzynarodowych (Darnley i in., 1995). Czołowe polskie laboratorium chemiczne powinno spełniać rolę koordynatora w zakresie analiz chemicznych, uczestniczyć w programach kalibracyjnych między laboratoriami krajowymi i zagranicznymi, organizować kursy specjalistyczne itp. Należy opracować normy w zakresie pobierania i przechowywania próbek oraz technik geoanalitycznych i zobligować stosowne instytucje do ich przestrzegania.
3. Pokrycie całego obszaru Polski mapami geochemicznymi w skali 1 : 100 000 lub 1 : 200 000.
4. Wykonanie szczegółowych map geochemicznych i biogeochemicznych dla obszarów potencjalnie toksycznych. Szczególny priorytet powinny mieć obszary o wysokiej koncentracji radonu w budynkach, arsenu, ołowiu i rtęci w glebach i wodzie pitnej, azotanów w wodach powierzchniowych oraz kadmu w roślinach uprawnych.
5. Prowadzenie monitoringu geochemicznego wód powierzchniowych i podziemnych. Szczególną uwagę należy zwrócić na stopień i zasięg skażenia wód na obszarach dawnej eksploatacji górniczej (Stewart & Severson, 1994).
6. Prowadzenie monitoringu geochemicznego i biogeochemicznego osadów rzecznych i jeziornych oraz odpowiednio ekosystemów lądowych i wodnych.
7. Rozwijanie badań geochemicznych osadów wybrzeża Bałtyku, celem zlokalizowania oraz prześledzenia wpływu naturalnych i antropogenicznych źródeł skażeń.
8. Wykorzystanie technik satelitarnych i lotniczych do określenia zasięgu skażeń atmosferycznych, wód powierzchniowych, gleb i skał, jak również zinventaryzowania roślinności i monitoringu zachodzących w nich zmian (Olhoeft, 1990; Watson & Knepper, 1994).
9. Dokonanie oceny zawartości pierwiastków śladowych w różnych złożach kopalin oraz ich wpływu na środowisko przyrodnicze. Powinna ona również obejmować analizę zasięgu formacji skalnych (wapieni, dolomitów, margli, opok, itowców, łupków ilastych, itp) neutralizujących kwasy (szczególnie siarkowy) lub stanowiących naturalny „kolektor” dla licznych pierwiastków potencjalnie toksycznych.
10. Identyfikacja naturalnych i antropogenicznych źródeł skażeń przy użyciu określonego spektrum pierwiastków śladowych lub składu izotopowego (Case & Krouse, 1980; Gough, 1993; King, 1995; Jackson i in., 1996; Hudson i in., 1997).
11. Opracowanie metod rekultywacji terenów górniczych lub obszarów skażonych.
12. Określenie koncentracji pierwiastków śladowych oraz związków organicznych (węglowodorów alifatycznych, wielopierścieniowych węglowodorów aromatycznych, polichlorobifenyli, fenoli, itp) dla różnych elementów abiotycznych i biotycznych na danym obszarze przed planowaną inwestycją. Pozwala to na dokonanie oceny jej przyszłego wpływu na lokalne środowisko przyrodnicze (Shacklette, 1990).
13. Prowadzenie badań nad procesami wietrzenia, w celu lepszego zrozumienia obiegu pierwiastków (Pavich, 1990).
14. Prowadzenie badań geochemicznych i biogeochemicznych w różnych aspektach geologii i ochrony środowiska (Kabata-Pendias, 1993; Migaszewski & Gałuszka, 1998).
15. Współpraca z międzynarodowymi zespołami badawczymi, celem dokonania porównań w skali globalnej. Powinna ona obejmować uczestnictwo w programach lub pracach następujących grup lub organizacji: International Geological Correlation Programme (Darnley i in., 1995), the Forum of European Geological Surveys Geochemistry Task Group (Plant i in., 1997), UNESCO oraz the International Union of Geological Sciences. Współpraca międzynarodowa powinna mieć najwyższy priorytet wśród realizowanych lub planowanych projektów badawczych.

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Należy podkreślić, że dopóty nie opracujemy odpowiedniej strategii badań w zakresie ochrony środowiska w Polsce, dopóki całkowicie nie zrozumiemy procesów geochemicznych i biogeochemicznych, zachodzących w najbardziej zewnętrznych warstwach Ziemi. Potrzeba rozwiązywania licznych problemów z pogranicza geochemii, biologii, rolnictwa i medycyny, pozwala przypuszczać, że przyszłość należy do badań biogeochemicznych.

Geochemistry plays an important role in all disciplines of geosciences including environmental science. The mentioned last describes interactions among terrestrial, atmospheric, aquatic, living and anthropogenic systems. The anthropogenic stress is a factor whose influence on natural environment has greatly increased lately. The most dangerous is the chemical aspect leading to degradation and destruction of land, water, air, and biota.

Environmental geochemistry is the study on the cycling and spatial distribution of elements in the Earth's outermost layers. This geoscience describes geochemical environment and dynamic processes that take place in it. They help us better understand all the potential hazards that can jeopardize a fragile nature balance.

This report presents an overview of environmental geochemistry exemplified by various case studies in Poland. Because of the pivotal position of geoanalysis, methods used in the Central Chemical Laboratory of the Polish Geological Institute in Warsaw have briefly been described. The key problems of biogeochemistry have been discussed in a separate report of this issue (Migaszewski & Gałuszka, 1998).

Principal objectives of environmental geochemistry

The principal objectives of environmental geochemistry are:

(1) To identify natural and anthropogenic sources of various chemical elements, especially those potentially detrimental or even toxic to the environment.

(2) To establish concentration ranges (baselines), as well as spatial and temporal distribution patterns of elements and organics in rocks, soils, sediments, surface- and groundwaters, plants, animals and man. Of great significance is water, a „conveyor” of many geochemical processes, containing various reactive soluble ingredients.

(3) To assess mobility, translocation and deposition of different elements and compounds in and between the media mentioned above.

(4) To investigate other geochemical characteristics, such as bioavailability of a specific elemental form, residence time of an element in various ecosystems, etc.

(5) To examine physico-chemical factors (pH, redox potential — E^0 , temperature, pressure, chemical composition, elemental interactions, etc.) the change of which can trigger or influence geochemical processes.

(6) To evaluate an impact of toxicants on various plant and animal species, man, and diverse ecosystems. This problem includes acid mine drainage, mine wastes, mine waters, mineral processing wastes, tailings, atmospheric emissions, and agricultural minerals (nitrogen, phosphate, potash, sulfur, zeolites).

(7) To identify „litho-environmental terranes” (Plumlee et al., 1994) — rock formations that have a particular impact on the environment, for example, carbonate series generate surface- and groundwaters with high acid-capacity, thus, mitigating the effects of acid mine drainage. Another exam-

ple is clays, claystones and clayey shales known as a sink for many trace elements.

(8) To work out mechanical or biological methods enabling removal or neutralization of toxicants.

The environmental geochemistry studies should also include geomorphology of the land, climatic and hydrologic variables, as well as bedrock, soil, flora and fauna characteristics. By studying geochemical processes, man can better understand environmental interactions, and prevent, reduce or eliminate their harmful effects on the environment.

A few notes on geochemical processes in the environment

Igneous, sedimentary and metamorphic rocks, as well as mineral deposits and mineralized zones, undergo weathering when exposed to atmosphere, hydrosphere and biosphere. The most important weathering factors are sun, water, temperature, oxygen, carbon dioxide and living organisms. Two basic types of weathering, i.e., the physical and the chemical, have been distinguished. The former leads to mechanical disintegration of rocks and minerals to smaller pieces and eventually to clay minerals, whereas the latter includes the following processes:

(i) dissolution — a process that converts a given mineral into water solution,

(ii) hydration — a reaction of a mineral with water leads to forming a hydrated mineral, for instance, hematite $Fe_2O_3 + H_2O \rightarrow$ goethite $Fe_2O_3 \cdot H_2O$,

(iii) hydrolysis — a process that consists in decomposition of minerals by water, for instance, kaolinitization of orthoclase — $2KAlSi_3O_8 + 3H_2O \rightarrow H_2Al_2Si_2O_8 \cdot H_2O + 4SiO_2 + 2KOH$, or its lateritization — $2KAlSi_3O_8 + 4H_2O \rightarrow 2Al(OH)_3 \cdot H_2O + 6SiO_2 + 2KOH$,

(iv) carbonatization — a process that leads to replacing in minerals various acids by carbonic acid, for instance, diopside $CaMg[Si_2O_6] + 2CO_2 \rightarrow$ dolomite $CaMg(CO_3)_2 + 2SiO_2$,

(v) oxidation-reduction — electron exchange reactions connected with addition/detachment of oxygen, for instance, oxidation of pyrite: (1) $FeS_2 + 3.5O_{2(aq)} + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$ or (2) $FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$ [this reaction is favored in the pH range from 2 to 7 producing eight times more acidity (Garrels and Thompson, 1960); at the pH less than 4 the bacterium genera *Thiobacillus* and *Leptospirillum* convert ferrous to ferric iron a million times faster than in the absence of these bacteria (Harrison, 1984)], or reduction of gypsum: $CaSO_4 \cdot 2H_2O + CH_4 \rightarrow H_2S + CaCO_3 + 3H_2O$ and further oxidation of hydrogen sulfide: $2H_2S + SO_2 \rightarrow 3S + 2H_2O$.

These processes form three groups of products:

(i) chemically unaltered minerals that are only subject to mechanical breakdown, for instance, garnet, zircon, rutile,

(ii) secondary minerals insoluble in water, for instance, iron, manganese and aluminum hydrous oxides and hydroxides,

(iii) weathering products dissolved in water, for instance, sodium, potassium, calcium, and other related elements.

The remaining geochemical processes that play an important role in diverse environmental systems are:

(i) biological activity — photosynthesis and other metabolic processes that involves transformation of nutrients including major (C, H, N, O, ...) and trace (B, Cu, Fe, Mn, Mo, ...) bioessential elements, along with non-bioessential elements (As, Be, Cd, Cr, Hg, Pb, ...),

(ii) radioactive decay — reactions that lead to forming radioactive elements combined with the release of α ($^{238}_{92}\text{U} \Rightarrow \alpha \Rightarrow ^{234}_{90}\text{Th}$), β ($^{87}_{37}\text{Rb} \Rightarrow \beta \Rightarrow ^{87}_{38}\text{Sr}$) and γ , or K-electron capture ($^{40}_{19}\text{K} \Rightarrow \text{K-electron capture} \Rightarrow ^{40}_{18}\text{Ar}$),

(iii) sorption of cations by negatively charged colloids (silica, clay minerals, organic matter), or anions by positively charged colloidal particles (iron, aluminum, cadmium, cerium and chromium hydroxides),

(iv) complexation and chelation (formation of complexes with a metal bonded to a ring structure) — ionic complexes play an important role in the transport of many elements, for instance, uranium $\text{UO}_2[\text{CO}_3]^{4-}_{3\text{aq}}$, lead $\text{PbCl}^{+}_{\text{aq}}$, copper $\text{Cu}^{+}_{5\text{aq}}$ $\text{Cu}[\text{CO}_3]^{2-}_{2\text{aq}}$ and probably noble metals,

(v) precipitation of various elements from water solutions in different aquatic systems including hydrothermal ones,

(vi) atmospheric emissions and deposition of elements by rainfall, or on dust particulates; they greatly influence both biotic and abiotic systems,

(vii) transport by water enables supplying or removing various chemical constituents.

Considering this, a specific element can be mobilized, transported, deposited, remobilized in many cycles as a result of changes in the pH and redox potential. These processes can be induced by mixing stream waters of different pH, seasonal influx of acid mine drainage waters, variations in rainfall-insolation pattern, supply of competitive elements, lithology of the study area (limestones, dolomites, claystones, siltstones and sandstones of different pH) or biological activity of bacteria, algae, plants or some animals, etc. Such elements as, As, B, Se and U are more mobile in alkaline soils and waters than in their acid equivalents, and *vice versa* Cd, Fe, Pb and Zn show greater mobility in acidic soils and waters. Moreover, anthropogenic elements reveal in soil greater mobility and bioavailability than their lithogenic or geologic counterparts.

One of many examples is iron that undergoes oxidation or reduction very easily. It is a very mobile element that quickly separates from other originally accompanying elements. In continental waters of pH 6 iron is about 100,000 more soluble than in sea waters of pH 8.5. This is the main reason why this metal is deposited at river mouths before it enters the sea. Iron oxides and hydroxides give a colorful spectrum (yellow through red) to rocks. In the presence of H_2S derived from magma or decayed organisms, iron forms sulfides. The most common mineral pyrite (FeS_2) is found in both hydrothermal systems and in various sedimentary facies. In wetlands, lakes and some parts of marine basins, in the presence of CO_2 , siderite (FeCO_3) nodules and concretions form. This mineral is also precipitated by bacteria. In the presence of phosphorus, blue vivianite [$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$] is formed. But the most important is the process of pyrite decomposition that gives iron sulfates and sulfuric acid. These two compounds lower the pH which consequently triggers a chain of redox reactions, for in-

stance, $2\text{PbS} (\text{galena}) + 2\text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O} + 3\text{O}_2 \rightarrow 2\text{PbSO}_4 (\text{anglesite}) + 4\text{FeSO}_4 + 2\text{H}_2\text{SO}_4$.

Geoanalytical techniques — the main tool of geochemistry

The most sophisticated geoanalytical methods include: inductively coupled plasma-mass spectrometry (ICP-MS) with laser ablation (LA-ICP-MS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), flame atomic absorption spectrometry (FAAS), X-ray fluorescence (XRF) and instrumental neutron activation analysis (INAA).

The attraction of ICP methods is the possibility to determine 20–60 elements simultaneously. The lowest detection levels of trace and major elements are obtained by ICP-MS technique. Its modification with laser ablation enables determining elements along selected microprofiles. The case study is determination of copper and zinc levels in tree rings from cottonwood (*Populus angustifolia* James) and aspen (*Populus tremuloides* Michx.) near Summitville, Colorado (King, 1995). In all ICP methods acid digestion by aqua regia (HCL-HNO₃) or „total” (HF-HClO₄-HNO₃-HCl) is required prior to analysis. Detection levels of elements can be lowered by preconcentration.

The FAAS method is not so „fast” as the multi-element ICP techniques; only one element at a time can be determined. Nonetheless, this method is much simpler and relatively free from interference. It is employed where flame atomisation is replaced by graphite furnace (ETA-AAS) or vapor generation/quartz tube modification, or when only a couple of elements are to be analyzed.

The XRF method is featured by a very precise measurement of major elements (Al, Ca, Fe, K, Mg, Na, Si, etc.), as well as some traces, i.e., Nb, Rb, Sr, Y and Zr. Determinations are performed on dry samples; this way disadvantageous acid digestion is avoided. According to the authors, this method can be widely applied to plants, especially to diverse plant and animal tissues that do not require ashing prior to analysis, for instance, tree leaves.

The INAA method is rarely employed. It is the best for rare earth elements (REE). Along with XRF, INAA belongs to non-destructive techniques, and samples can be used for other analyses, or archived. However, samples cannot be transported or otherwise employed before „cooling down”.

Organics are determined using gas chromatography. New models of gas chromatograph are equipped with a mass spectrometer detector (PAHs, phenols) or an electron capture detector (PCBs and organochlorine pesticides). Organics in waters are determined by liquid chromatography.

Stable-isotope techniques are widely applied to environmental geochemistry (Spiker, 1990). Of particular importance are determinations of stable sulfur isotopes (^{34}S relative to ^{32}S) (Krouse, 1977, 1978; Case & Krouse, 1980; Herzig et al., 1989; Nriagu & Glooschenko, 1992; Jackson et al., 1996; Migaszewski & Pałowski, 1996; Migaszewski, 1997, 1998b) and lead isotopes (^{204}Pb , ^{206}Pb , ^{207}Pb , ^{208}Pb) (Jaakkola et al., 1983; Church, 1993). They enable pinpointing pollution sources. Sulfur isotopes are most widely used in environmental geochemistry. They are determined on SO_2 with a mass spectrometer. The most updated models are combined with laser ablation.

In case of soils, additional physico-chemical parameters including cation exchange capacity (K^+ , Na^+ , Ca^{2+} , Mg^{2+}), grain-size distribution, porosity, ignition loss, pH, total inor-

ganic carbon (TIC), total organic carbon (TOC) are also determined.

Morphology of mineral grains and airborne particulates, or development of chlorosis and/or necrosis in plants are examined under optical or electron microscopes. The content of various mineral phases in soils and dusts are determined with an X-ray diffraction method. The spatial distribution of elements on a microscale is determined with an electron microprobe (Manninen et al., 1995). Rocks are examined using different petrographic techniques.

The Central Chemical Laboratory of the Polish Geological Institute performs analyses of minerals, rocks, soils, sediments, waters, stack ashes, fuel, feedstock, vegetation and meat using the following methods (in parentheses elements and compounds determined by each technique are given):

(1) ICP-AES (Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sc, Si, Sn, Sr, Ti, V, Y, Yb, Zn, Zr),

(2) FAAS (Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Se, Si, Sn, Sr, Ti, V, Zn, Zr); ETA-AAS (As, Cd, Hg, Pb, Se for rocks, soils, sediments and vegetation),

(3) XRF (Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sc, Se, Si, Sn, Sr, Ti, V, Y, Yb, Zn, Zr),

(4) classical chemical analyses that include:
— gravimetric method (SO₂, S),
— spectrophotometry (Fe, Mn, Mo, Th, Ti, W, Zr, exchanged cations),
— complexometric titration (Al, Ca, Mg),
— ion selective electrode method (F),
— pH measurement,
— coulometric titration (C, S),

(5) gas chromatography (hydrocarbons, PCBs, phenols and pesticides in solid materials),

(6) liquid chromatography (PAHs, phenols and pesticides in waters),

(7) infrared spectrometry (crude oil derivative extracts).

Elemental detection limits for rocks, soils, sediments, vegetation, and waters obtained in the CChL in Warsaw have been presented in tables 1 and 2.

The modern instrumentation, wide spectrum of applied analytical techniques, highly trained and experienced staff, participation in interlaboratory calibration programs rank CChL in Warsaw among „the cream of the crop” (Migaszewski, 1998a).

Environmental geochemistry and biogeochemistry projects carried out in the Polish Geological Institute

Geochemistry and biogeochemistry are a keystone of environmental geosciences. These two disciplines are also applied in agriculture and medicine. The Polish Geological Institute, as a leading research branch of the Geological Survey of Poland, takes part in many environmental projects. The most spectacular are geochemical atlases (scale 1 : 50,000 through 1 : 500,000) of soils, sediments and waters produced for the selected urban-industrial areas of Poland (including

Tab. 1. Detection limits of elements in rocks, soils, sediments and vegetation obtained in the Central Chemical Laboratory of the Polish Geological Institute in Warsaw

Chemical element	Measurement unit	Detection limit			
		ICP-AES	WD-XRF	FAAS	ETA-AAS
Ag	ppm ($\mu\text{g g}^{-1}$)	1	—	0.5	—
Al	%	0.01	0.01*	0.01	—
As	ppm	5	2	0.05 (HG-AAS)	0.05
B	ppm	1	—	—	—
Ba	ppm	1	5	5	—
Be	ppm	1	—	0.5	—
Ca	%	0.01	0.01*	0.005	—
Cd	ppm	0.5	5	0.5	0.005
Co	ppm	1	3	1	—
Cr	ppm	1	3	1	—
Cu	ppm	1	3	1	—
Fe	%	0.01	0.01*	0.005	—
Hg	ppb ($\mu\text{g kg}^{-1}$)	—	500	5 (CV-AAS)	10
K	%	0.01	0.01*	0.01	—
La	ppm	1	5	—	—
Li	ppm	10	—	1	—
Mg	%	0.01	0.01*	0.01	—
Mn	ppm	1	10*	1	—
Mo	ppm	5	2	10	—
Na	%	0.01	0.01*	0.01	—
Ni	ppm	1	3	1	—
P	%	0.005	0.005*	—	—
Pb	ppm	3	3	2	0.05
S	%	0.005	0.01*	—	—
Sc	ppm	1	3	—	—
Se	ppb	—	300	5 (HG-AAS)	10
Si	%	0.01	0.01*	0.01	—
Sn	ppm	5	2	10	—
Sr	ppm	1	2	1	—
Ti	%	0.001	0.01*	0.01	—
V	ppm	1	3	10	—
Y	ppm	0.5	2	—	—
Yb	ppm	0.5	2	—	—
Zn	ppm	1	2	1	—
Zr	ppm	1	1	10	—

ICP-AES — inductively coupled plasma-atomic emission spectrometry, WD-XRF — wave length dispersive-X-ray fluorescence (fusion*/pellets), FAAS — flame atomic absorption spectrometry, ETA-AAS — electro-thermal atomization-atomic absorption spectrometry, CV-AAS — cold-vapor atomic absorption spectrometry; HG-AAS — hydride generation atomic absorption spectrometry

NOTE: (i) for rocks, soils, sediments: 1 g of sample per 50 ml of solution

(ii) for vegetation: 0.5 g of ash per 50 ml of solution

general geochemical atlas of Poland, 1 : 2,500,000). So far eight of them have been made including: Warsaw (Lis, 1991), Warsaw and Environs (Lis, 1992), Kielce (Lenartowicz, 1994), Poland, Cracow and Upper Silesia (Lis & Pasieczna, 1995a-c), Wałbrzych (Pasieczna, Siemiątkowski & Lis, 1995) and Polish-Lithuanian cross-border area (Atlas, 1997). In addition, two atlases encompassed sediments of the southern Baltic Sea, 1 : 500,000 (Szczepańska & Uścińowicz, 1994) and the Vistula Lagoon, 1 : 100,000 (Uścińowicz & Zachowicz, 1996). Three radioecological atlases of Poland, 1 : 500,000 and 1 : 200,000, including U, Th, K, Ce and γ , were produced, too (Strzelecki et al., 1993, 1994, 1995).

The geochemical investigations also include monitoring of stream and lake sediments of Poland carried out since 1990 (Bojakowska & Sokołowska, 1996a-c). Its scope en-

Tab. 2. Detection limits of cations and anions in waters obtained in the Central Chemical Laboratory of the Polish Geological Institute in Warsaw

Cations Anions	Measurement unit	Detection limit			
		ICP-AES	FAAS	ETA-AAS	Other methods
Al	mg/l	0.05	0.05	0.002	—
As	mg/l	0.05	0.0005(HG-AAS)	—	—
B	mg/l	0.03	—	—	—
Ba	µg/l	1	100	—	—
Ca	mg/l	0.1	1	—	—
Cd	µg/l	3	5	0.1	—
Co	µg/l	8	20	1	—
Cr	µg/l	4	20	0.5	—
Cu	µg/l	5	10	1	—
Fe	mg/l	0.01	0.02	—	—
Hg	µg/l	—	0.5 (CV-AAS)	—	—
K	mg/l	0.3	0.01	—	—
Li	mg/l	0.02	1	—	—
Mg	mg/l	0.05	0.01	—	—
Mn	µg/l	1	10	0.4	—
Na	mg/l	0.2	0,01	—	—
Ni	µg/l	10	20	1	—
P	mg/l	0,2	—	—	1 (HPLC) (PO ₄)
Pb	mg/l	0,05	0,03	1	—
S	mg/l	0,1	—	—	1 (HPLC) (SO ₄)
Se	µg/l	—	1 (HG-AAS)	—	—
Si	mg/l	0,3	—	—	—
Sn	µg/l	10	—	—	—
Sr	µg/l	1	10	—	—
Ti	µg/l	5	—	—	—
V	µg/l	6	100	3	—
Y	µg/l	0,5	—	—	—
Zn	µg/l	5	10	—	—
Br	µg/l	—	—	—	100 (HPLC)
Cl	mg/l	—	—	—	1 (HPLC)
F	µg/l	—	—	—	100 (HPLC)
N (NO ₃)	µg/l	—	—	—	10 (HPLC)
N (NO ₂)	µg/l	—	—	—	10 (HPLC)
NH ₄	µg/l	—	—	—	50 (SPF)

ICP-AES — inductively coupled plasma-atomic emission spectrometry, FAAS — flame atomic absorption spectrometry, ETA-AAS — electro-thermal atomization-atomic absorption spectrometry, CV-AAS — cold-vapor atomic absorption spectroscopy; HG-AAS — hydridegeneration atomic absorption spectrometry; HPLC — high pressure liquid chromatography; SPF — spectrophotometry

compasses determinations of trace and major elements, as well as PAHs. The other stream sediment geochemistry program dealt with elemental ratios in alluvial sediments of the Kamienna River (Holy Cross Mts) (Lenartowicz, 1995).

Quality of groundwaters in Poland has been monitored since 1991 (Hordejuk, 1996). Furthermore, two groundwater regional monitoring programs (for Kielce and Tarnobrzeg provinces) have been conducted by the Świętokrzyskie Mts Branch of PGI in Kielce (Prażak, 1996).

The same Branch has pioneered regional geochemical and biogeochemical investigations in Holy Cross Mountain National Park and surrounding areas (Migaszewski & Paślawski, 1996; Migaszewski, 1997, 1998a, b). Chemical and isotopic (sulfur) analyses were done on rocks, soils, vegetation (lichen thalii, moss tissues, pine needles), spring waters, and stack ash, fuel and feedstock from major local industrial facilities. Aside from over 30 major and trace elements, organics (PAHs, PCBs, phenols, pesticides) in soils and plant materials were determined, too (Migaszewski et al.,

1996; Migaszewski, 1998c). These studies have been carried out in cooperation with the US Geological Survey.

All the chemical analyses have been done in the Central Chemical Laboratory of PGI in Warsaw, whereas sulfur isotope determinations at Institute of Physics of Maria Curie-Skłodowska University in Lublin.

Future development of environmental geochemistry in Poland

There is no systematic environmental assessment and mitigation strategy in Poland. The same concerns geochemical and biogeochemical studies. Considering the present status of environmental geochemistry in Poland, some conclusions can be drawn. First of all, most of the projects deal only with narrow-scope problems; comprehensive studies are scarce. Furthermore, different methods and incoherent methodology used by various research groups often makes impossible any comparisons. But, the greatest disadvantage seems to be ingrained in the lack of cooperation between geochemists, geologists, chemists, biologists, soil and forest scientists, and geophysicists or isotope physicists. The studies have been conducted separately and conclusions derived from the results obtained are incomplete and distorted. The key for a successful progress in environmental geochemistry in Poland lies in overcoming this psychological „threshold”.

A spectrum of visible concerns linked to redistribution of toxicants has become clear to the American

public recently. Many agencies, including the US Geological Survey, have been working on the coherent strategy of environmental geochemistry development (Filipek, 1990). In Poland such programs should be incorporated into the strategic policy of the Ministry of Environmental Protection, Natural Resources and Forestry. The main problems that need to be solved are:

(1) To establish and develop a national geochemical and biogeochemical database for concentrations of elements and organics in soils, stream, lake and marine sediments, rocks, surface- and groundwaters, and at least partly plant bioindicators, in relation to geologic, topographic, hydrologic, biologic, climatic, and present land-use variables (Manahan, 1994). It also should be a part of a global geochemical and biogeochemical database for environmental and resource management (Darnley et al., 1995).

(2) To work out uniform methods and methodology of collecting samples, sample preparation and geoanalyses according to international requirements (Darnley et al., 1995).

The leading Polish laboratory should perform control analyses, participate in interlaboratory calibration projects, supply other labs with standards, organize training courses, etc. A quality-assurance program and quality-control procedures should be instituted for the collection, preservation, storage, and geoanalyses of all samples.

(3) To cover the whole area of Poland with geochemical maps, scale 1 : 100,000 or 1 : 200,000 including the media mentioned above (1).

(4) To produce detailed geochemical and biogeochemical maps for particularly toxic „spots”. The priority ought to be given to areas of high indoor radon levels, arsenic, lead and mercury in soils and drinking water, nitrates in surface waters, or cadmium in crops.

(5) To monitor geochemical changes in surface- and groundwaters; a special attention should be paid to the level and extent of water contamination associated with historically mining areas (Stewart & Severson, 1994).

(6) To conduct geochemical and biogeochemical monitoring of stream and lake sediments, along with terrestrial and aquatic wildlife ecosystems. Stream sediment geochemical data provide an indication of trace element concentrations in soils, crops and forage. Such data can be used for identifying areas potentially toxic to grazing livestock.

(7) To develop the Baltic offshore geochemistry for tracing natural and anthropogenic (industrial effluents and sewage outfalls) variations.

(8) To put to use broad-scale satellite and airborne techniques in environmental geochemistry studies to map contamination plumes or a variety of water quality parameters in surface water systems, to inventory and monitor vegetation and areas of vegetation stress, and to delineate land-use pattern (Olhoeft, 1990; Watson & Knepper, 1994).

(9) To evaluate the potential for trace element signature of mineral deposits and to make mineral resource-environment assessment for application in land-use management. It should encompass spatial distribution of acid-buffering or toxicant-sinking carbonate and clayey-silty formations.

(10) To identify and examine potential natural and anthropogenic sources of pollution (Gough, 1993; King, 1995; Hudson et al., 1997). They would include acid mine drainage, application of agricultural and industrial minerals, mining and processing activity, influence of hazardous waste sites, etc. All these data should also be contained in the national database.

(11) To work out methods for reclaiming mine lands and remediating polluted areas.

(12) To assess geochemical and biogeochemical baselines for non-bioessential or hazardous elements, or organics in a given area prior to construction of a mine or an industrial plant in order to monitor their future impact on various environmental systems (Shacklette, 1990).

(13) To perform weathering-process research to better understand the cycling of elements (Pavich, 1990).

(14) To carry out combined environment- and issue-oriented geochemical and biogeochemical research in different aspects (Kabata-Pendias, 1993; Migaszewski & Gąsuzka, 1998).

(15) To cooperate with environmental groups from different countries to make global environmental geochemistry assessments. This cooperation should include a joint activity through the International Geological Correlation Programme (Darnley et al., 1995), the Forum of European Geological Surveys Geochemistry Task Group (Plant et al., 1997), UNESCO and the International Union of Geological

Sciences. The international and interdisciplinary projects need to be given the highest priority.

It should be underscored here that **no environmental strategy in Poland can exist until we completely understand geochemical and biogeochemical processes occurring at and near the Earth's surface.** The practical aspects of investigations performed in the Holy Cross Mts indicate that the future „point of gravity” will be shifted toward biology, agriculture and medicine, converting the environmental geochemistry into the environmental biogeochemistry.

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