

# A review of geochemical background concepts and an example using data from Poland

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Received: 22 August 2006 / Accepted: 18 September 2006 / Published online: 17 October 2006  
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**Abstract** One of the most crucial issues of recent environmental sciences is the topic of background concentrations of elements and organic compounds in various abiotic and biotic systems. The relationship between natural and anthropogenically altered concentrations of chemical species is a question that involves many implications in the geosciences, environmental and biological sciences, toxicology, and other related disciplines. This is especially important when interpreting geochemical and biogeochemical anomalies of toxic elements and/or organic compounds in various media. To better understand the potential impact of hazardous substances in the environment, we must become more familiar with their spatial and temporal distribution and with their behavior under different physico-chemical and biotic conditions. This review presents an assessment of the geochemical background concept as used by various authors. Different assumptions and approaches to this topic are presented, including direct, statistical, and integrated methods. Based on the results derived from geochemical and biogeochemical studies performed in selected forest ecosystems of Poland, an integrated method is presented. As a consequence of data processing, a normal distribution of data points was obtained using an iterative  $2\sigma$ -technique. This method of estimating geochemical background is feasible and can be used for

setting environmental quality standards or for studying the impact of anthropogenic pollution sources on the environment.

**Keywords** Geochemical background · Definitions · Methods · Integrated assessment · Forest ecosystems

## Introduction

Since the onset of human civilization, man has influenced the environment. This influence has assumed various forms, originally mostly physical, then gradually chemical or both. This trend was actually expedited in prehistoric times with the beginning of primitive smelting of copper, lead, tin, and iron. The heat processing of metal ore and burning of charcoal released substantial amounts of pollutants to the environment. It is worth mentioning that raised levels of lead dating back to ancient Greek and Roman period were found in Greenland ice cores (Hong et al. 1994), as well as, copper dating from Roman and medieval times (Hong et al. 1996). Nonetheless, the pollution level was relatively low and nearly all the media revealed a minimum human impact. All this changed rapidly with the onset of the so-called “industrial revolution” that took place in Europe in the mid nineteenth century (e.g., Nriagu 1979; Boutron et al. 1995; Mannion 2002). Consequently, the present surface environment shows combined natural and anthropogenic imprints. The results derived from many studies have indicated a considerable rise in the concentration of heavy metals and organic compounds in different media compared to the “pre-industrial” period (e.g., Villeneuve and Holm 1984; Richardson

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1992). This increase is well documented in sediments (e.g., Aston et al. 1973; Gschwend and Hites 1981; Baudo et al. 1990; Gałuszka and Migaszewski 2004).

Based on these and other studies, the principal question is—what concentration is natural (geologic and/or biologic) and what concentration is non-natural (anthropogenic)? The answer to this question involves the definition of geochemical background, and has stirred a lot of controversy and discussion since the beginning of studies involving environmental geochemistry and biogeochemistry. Geochemists cannot reach a consensus as to a precise definition as well as a coherent method for assessing geochemical background in the surface environment (Tobías et al. 1997; Matschullat et al. 2000; Baize and Sterckeman 2001; Portier 2001; Li et al. 2003). The discrepancy in assumptions, approaches, and methods is primarily due to the spatial and temporal variability of background concentrations, and the diverse geochemical properties of a given substance and its matrix (e.g., Smith and Huyck 1999; Kabata-Pendias and Pendias 2001). It is interesting to note that geologists may also have problems with determining elemental background concentrations in unweathered rocks, especially when the rocks are formed in heterogeneous environments. This issue becomes even more complex when these rocks are subsequently subjected to metamorphic, hydrothermal, or weathering processes. Moreover, our knowledge of the rock-type ratio in the Earth's crust is inadequate because it is lithologically and petrologically variable and poorly exposed. This is the main reason why different authors give various Clarke values for the entire Earth's crust and individual rock formations or rock types (e.g., Turekian and Wedepohl 1961; Bowen 1979; Levinson 1980; Rickwood 1983; Fortescue 1992).

The establishment of background concentrations in the surface environment is important for at least two reasons: (1) it allows the distinction of contaminated or polluted areas (or concentrations of elements and organic compounds that are regarded as pollutants) from uncontaminated or unpolluted ones, and (2) it enables modeling of the anthropogenic influence on the mobilization, migration, and deposition/uptake of substances in the environment. The first objective may be useful for setting environmental quality standards, whereas the second one is useful for assessing the extent of human activities and their influence on the cycling of elements. Of the different methods, the integrated one seems to provide a good assessment of the geochemical background. This article presents the iterative  $2\sigma$ -technique used for calculating concentrations of seven elements (Cu, Fe, Hg, Mn, S, Sr, and Zn) in the soil horizons-O, -A and -B, and 1- and 2-year-old

Scots pine (*Pinus sylvestris* L.) needles derived from three selected national parks located in northeastern, south-central and southeastern Poland.

#### **“Background,” “baseline,” and related terms: different assumptions and approaches**

Most of the specialists who investigate “geochemical background” use this term without providing precise definition. Geochemical background is understood mainly as a natural value for a given medium not impacted by anthropogenic activities (Gough 1993). In contrast, it is interesting to note that exploration geochemists refer to a non-anomalous element concentration as a background (Plumlee 1999). A similar definition of the geochemical background is given in the Dictionary of Geological Terms (Bates and Jackson 1984): “*In geochemical prospecting, the range in values representing the normal concentration of a given element in a material under investigation such as rock, soil, plants, and water.*” In other words, it is a reference level to anomalous element concentrations in a mineral deposit (Selinus and Esbensen 1995). Considering the practical implications, the background value in exploration geochemistry is usually higher than in environmental geochemistry, because it may be influenced by both natural and anthropogenic concentrations. There are also other synonymous or equivalent terms to geochemical background. Some of the authors (e.g., Baize and Sterckeman 2001) apply the term “pedo-geochemical background” in relation to natural concentrations of elements in soils. However, the application of this term should also be discussed considering every aspect of the necessity for dividing background concentrations into parts associated with different environmental samples.

The Kentucky Guidance for Ambient Background Assessment (2004) distinguishes between “natural background” and “ambient background.” The first is defined as “*the amount of naturally occurring substances in the environment, exclusive of that from anthropogenic sources*” and the second as “*the concentrations of naturally occurring inorganic substances and ubiquitous anthropogenic inorganic substances in the environment that are representative of the region surrounding the site and not attributable to an identifiable release.*” It is easy to note that “natural background” in this definition is synonymous with “geochemical background.”

In other US governmental documents, the term “background” is dissimilar to that discussed in the previous paragraphs. For example, in the Model Toxics

Control Act—Cleanup (2001) two terms are distinguished: (1) “area background” defined as: “*the concentrations of hazardous substances that are consistently present in the environment in the vicinity of a site which are the result of human activities unrelated to releases from that site,*” and (2) “natural background” specified as: “*the concentration of hazardous substance consistently present in the environment that has not been influenced by localized human activities.*” These definitions limit the background to hazardous substances only. The first definition is similar to “anthropogenic background” used by Portier (2001): “*concentrations typically observed in a region that are the result of human activities but that are not associated with a specific contamination activity.*”

One of the most interesting methodological approaches to this subject was presented by Matschullat et al. (2000). These authors emphasize the lack of a clear definition and define background as: “*a relative measure to distinguish between natural element or compound concentrations and anthropologically influenced concentrations in real sample collectives.*” Any carefully phrased definition requires, however, some more information on the method of how background is determined. At the “Interdisciplinary Research in Environmental Protection” conference held in Poland in 2005, a new definition of geochemical background was presented: “*Geochemical background is a theoretical ‘natural’ concentration of a substance in a specific environmental sample (or medium), considering the spatial and temporal variables, which may be determined with direct, indirect, and integrated methods*” (Gałuszka 2005, 2006). The different methods used for assessing the geochemical background are discussed in the next section.

There are other critical issues regarding background concentrations that should be considered. One of the most important is how can we use this term—can we calculate it for each medium of the surface environment? In the author’s opinion, it is impossible to obtain accurate background concentrations for air and natural water due to high spatial and temporal variability of these media, as well as the dependence on many unpredictable factors of both natural (climatic, geologic, and biologic) and anthropogenic origin. Of these two media, the atmosphere shows particularly dynamic changes in its chemistry. The long-range transport of airborne pollutants, released from natural (soil and rock erosion, volcanic eruptions, and biological processes) and anthropogenic sources, enriches water and soil with different elements even in relatively clean areas (Nriagu 1989). A similar problem concerns plants, especially those used as bioindicators for

assessing environment quality. There are numerous, sometimes unpredictable, physico-chemical and biological factors that influence vegetation even in pristine areas. These factors are closely linked to a response of a particular organism to different topographic (elevation, aspect), climatic (insolation, wind, pressure systems, and moisture), hydrologic, and edaphic (soil moisture, texture, pH, etc.) conditions, not to mention physiologic and genetic parameters. The interaction of these factors represents a true “roulette”, because chance too can have a major influence (Migaszewski et al. 2001). Differences in concentrations of elements between spring and fall samples from the same species can exceed a factor of ten (Dunn et al. 1992). Some of the plant species or their organs can accumulate substances in large amounts (Dunn et al. 1992; Anderson et al. 1999; Gałuszka 2005, 2006) or produce some of them, for example phenols are produced by Scots pine needles (Migaszewski et al. 2002).

An assessment of background concentrations in abiotic solid samples (i.e., rocks, sediments, and soils) may seem easier than biologic materials, but it should be employed with some caution, and an awareness of complex processes that influence the chemistry of samples (sorption, degradation, pH, biogenic transformations, etc.). Some of the trace elements, for example As, Hg, Pb, Se, Sn, may undergo microbial-mediated methylation and demethylation and be partly removed from a given medium (e.g., Herring 1991; Kabata-Pendias and Pendias 2001). The situation is even more confusing when assessing concentrations of most of the organics, like polynuclear aromatic hydrocarbons, phenols, etc. We still do not know what part of a specific organic compound is a metabolic product or is linked to a discharge of “reworked” man-made organics. Moreover, the processes of sorption, biodegradation, biomethylation, and biodemethylation play an even more important role here, especially in aquatic ecosystems (D’Itri 1990).

Another crucial issue that ought to be considered, when comparing results from different sampling periods or remote areas, is the use of the identical collecting and preparation procedures, as well as analytical methods and techniques (Matschullat et al. 2000; Salminen and Tarvainen 1997; Salminen and Gregorauskiene 2000). In one example, Ramsey et al. (1992) reported that 80% of the total variance was linked to natural geochemical variance, 16% to sampling, and 4% to geochemical analyses.

Another term “geochemical baseline” is closely associated with “geochemical background” and they are often used as synonyms (e.g., Nieto et al. 2005). Originally, it was used by Tidball et al. (1974) in a

study on the influence of a coal-fired powerplant on the environment in the Powder River Basin (Montana and Wyoming). These authors distinguished geochemical baselines as a natural background in a heavy anthropogenically polluted area. The baselines were expressed as a 95% expected concentration range and were calculated as  $GM/GD^2$  to  $GM \times GD^2$  (where  $GM$  = geometric mean and  $GD$  = geometric deviation). Those samples with element concentrations distributed outside of 95% range were recognized as representing environmental pollution. These values can be used for future monitoring studies, provided that the newly collected samples are of the same soil horizon, sediment depth, plant part etc., and that they are collected, prepared and analyzed by methods comparable to those used in previous studies (e.g., Gough et al. 1988a, b; Crock et al. 1992; Migaszewski et al. 2004, 2005). A somewhat different approach was made in a study in Alaska near Denali National Park (Gough and Crock 1997), where all element concentration values beyond about 6 km from a coal-fired power plant were considered regional baselines because plant and soil samples appeared to be outside the zone of measurable industrial influence.

According to Darnley (1995), “geochemical baselines” are concentrations of substances characterizing variability in the geochemistry of the Earth’s surface materials and are needed for “*documenting the present state of the surface environment and to provide datum against which any changes can be measured.*” Another definition of baseline is given by Lee and Helsel (2005). These authors define the baseline as “*a summary of existing conditions over some time frame for some environmental system, or material of interest.*” The baseline concentrations, usually expressed as an observed or 95% expected range, represent a measure of a given sample in a specific location and time. They vary in areas of different pollution, but in pristine areas, geochemical baseline concentrations are close to background values. Baseline studies enable us to assess chemical pattern changes in the environment resulting from human activities. That is why, in most countries, they are usually conducted to assess the state of natural ecosystems prior to implementation of a specific investment, for example construction of mines, power plants, dams, airports, etc. However, some authors (e.g., Reimann and Garret 2005) do not support the use of the term “baseline.” Background or baseline studies should encompass basic information on the composition of sampled material, extent and intensity of geochemical and geological processes, as well as the influence of different environmental and biological factors.

There is another issue often omitted in many publications. The discharge of anthropogenic pollutants into the environment is not necessary in order to change the chemistry of different media. The same effect may be produced as a result of physical (mechanical) activities, for example, by removing an insulating rock cover and exposing a metal sulfide zone. Weathering of pyrite and associated sulfide minerals may lead to a distinct decrease of pH and the release of heavy metals to the environment (e.g., Agarwal 1975; Reichenbach 1994; Nordstrom et al. 2000).

### Methods of assessing background concentrations

There are two major methods used for assessing background concentrations (Matschullat et al. 2000): (1) direct (geochemical) and (2) indirect (statistical). The first method, also known as empirical method, refers to studies of samples not affected by industrial activities or to relatively pristine sites (Crommentuijn et al. 2000; Baize and Sterckeman 2001; Horckmans et al. 2005). The samples of this method encompass, for example, deep limnic, marine, overbank, and river sediments, archival plants from herbaria, deep soil horizons, tree rings, glacial ice cores, or others collected from relatively pristine areas. In these studies, the background concentrations are usually presented as mean or median values. An example of such an approach is the study conducted by Kelley and Taylor (1997) in mineralized areas of Alaska, in which natural waters from undisturbed (unmined) areas were selected as background samples. The geochemical methods of this type of study are often criticized as having subjective sample selection criteria, high costs, and heavy laboratory workload.

In contrast, far more popular statistical methods have been used not only for assessing background concentrations, but also for the separation of geochemical anomalies from geochemical background. Of the different methods, regression analysis (partial least squares regression analysis) (Selinus and Esbensen 1995), fractal method (Li et al. 2003), and probability plots (Tobías et al. 1997) have commonly been applied. The other statistical approach is to eliminate the outliers that are considered to be anthropogenically influenced, thus creating more normal distribution. These statistical methods for background assessments are discussed in more detail by Matschullat et al. (2000). These authors selected three of the tests ( $4\sigma$ -outlier test, iterative  $2\sigma$ -technique and calculated distribution function), tested for accuracy, and found

them adequate for quantification of geochemical background.

The most interesting of all is an integrated method combining both a direct and indirect approach. The idea of this method is that samples should be collected in pristine areas, restricting purposely the range of obtained data. In the author's opinion, mature forests representing ecologically the most stable ecosystems that are shaped by balanced outflow and inflow of matter and energy are the most promising for detailed geochemical studies. The same view is shared by Horckmans et al. (2005): "occurrence of an adult population of trees was assumed to ensure that the soils have not been disturbed, at least for the lifetime of such a tree."

The iterative  $2\sigma$ -technique presented by Matschullat et al. (2000) is also a feasible method of background assessment. It corresponds well to commonly used threshold (baseline) calculations with the formula: upper limit of mean  $\pm 2\sigma$  range (e.g., Li et al. 2003). In some of the datasets, with nearly normal distributions, baseline and background values are the same in this approach.

Based on the results derived from geochemical studies of soils and plant bioindicators from three Polish national parks (archival data partly presented in Migaszewski et al. 2004, 2005), an attempt was made to assess geochemical background by using an iterative  $2\sigma$ -technique.

### Integrated geochemical background assessment for three national parks in Poland

#### Scope of investigations

An assessment of chemical variability in forest ecosystems of three selected national parks in Poland, i.e., Magurski (MNP), Świętokrzyski (ŚNP), and Wigierski (WNP) (Fig. 1), was performed in the spring of 2002. The chemical determinations included 30–40 trace elements in the soil horizons-O (Ol + Ofh), -A, and -B (or -E), 1- and 2-year-old, i.e., 2001 and 2000, Scots pine (*P. sylvestris* L.) needles, Scots pine bark and *Hypogymnia physodes* (L.) Nyl. thalli (lichen). These studies showed that variability for elements in soils and plant bioindicators of WNP is primarily governed by bedrock lithology and to a lesser extent by anthropogenic factors; the two remaining parks revealed a more distinct anthropogenic imprint, except for a small enclave in the northeastern part of ŚNP where Ni and Mn anomalies associated with scattered metallic mineralization occur. Determinations of stable sulfur isotopes



**Fig. 1** Location of the study areas within three national parks of Poland

in needles, and a SEM study of airborne particulates on pine needles, confirmed a diverse anthropogenic influence on the ecosystems examined (Migaszewski et al. 2004, 2005). The most interesting of all the parks examined was WNP, because this area has experienced lower levels of air pollution relative to other parts of Poland.

It should be stressed that the results (including a much wider range of chemical and isotopic determinations) were published and interpreted, but not in terms of geochemical background assessment. This comprehensive study gave a unique opportunity to compare the background values calculated for areas of different anthropogenic impact and geology. In addition, the samples were collected in the same vegetative season and soils from the same horizons, obeying all the procedures required, as well as prepared and analyzed using similar methods and techniques. The geochemical and biogeochemical studies in the Holy Cross Mountains (south-central Poland) have been carried out by the same field and laboratory teams since 1994. This produces a unique opportunity to compare the results derived from different investigation phases.

#### Brief outline of study areas and methods

The MNP investigation sites were located within the Magura Nappe composed of flysch sediments (sandstones with clayey shale interbeds). The spectrum of soil types includes rankers, and gray and brown soils (Migaszewski et al. 2004). The prevailing rock types in ŚNP are Middle and Upper Cambrian quartzitic sandstones and siltstones with clayey shale interbeds,

**Table 1** Summary statistics for Cu, Fe, Hg, Mn, S, Sr, and Zn in the soils and Scots pine needles at Wigierski (WNP), Świętokrzyski (ŚNP) and Magurski (MNP) National Parks

Park	Medium	Cu (mg kg <sup>-1</sup> )	Fe (mg kg <sup>-1</sup> )	Hg (mg kg <sup>-1</sup> )	Mn (mg kg <sup>-1</sup> )	S (mg kg <sup>-1</sup> )	Sr (mg kg <sup>-1</sup> )	Zn (mg kg <sup>-1</sup> )
<b>WNP</b>								
<i>n</i> = 22	O	AM 7	AM 1,442	AM 0.10	AM 910	AM 1,016	AM 12	AM 50
		GM 7	GM 1,030	GM 0.10	GM 761	GM 984	GM 11	GM 46
		Med. 6.5 SD 3	Med 1,284.5 SD 1,080	Med. 0.10 SD 0.039	Med. 747 SD 592	Med. 1,048 SD 247	Med. 9.5 SD 8	Med. 44.5 SD 22
<i>n</i> = 12	A	AM 4	AM 6,283	AM 0.06	AM 599	AM 487	AM 15	AM 28
		GM 3	GM 5,706	GM 0.05	GM 491	GM 272	GM 7	GM 21
		Med. 3 SD 3	Med. 5,950 SD 2,718	Med. 0.05 SD 0.028	Med. 466 SD 387	Med. 205 SD 683	Med. 4 SD 21	Med. 18 SD 8
<i>n</i> = 7	B	AM 3	AM 8,186	AM 0.02	AM 300	AM 66	AM 5	AM 19
		GM 3	GM 7,529	GM 0.02	GM 237	GM 57	GM 4	GM 18
		Med. 3 SD 2	Med. 6,700 SD 4,122	Med. 0.02 SD 0.01	Med. 208 SD 243	Med. 70 SD 33	Med. 4 SD 4	Med. 18 SD 8
<i>n</i> = 15	N1	AM 4	AM 52	AM 0.02	AM 505	AM 881	AM 3	AM 37
		GM 4	GM 52	GM 0.02	GM 466	GM 877	GM 3	GM 36
		Med. 4 SD 1	Med. 49 SD 9	Med. 0.02 SD 0.004	Med. 505 SD 156	Med. 872 SD 79	Med. 3 SD 0.004	Med. 36 SD 7
<i>n</i> = 15	N2	AM 4	AM 58	AM 0.03	AM 682	AM 837	AM 4	AM 34
		GM 4	GM 57	GM 0.03	GM 622	GM 835	GM 4	GM 33
		Med. 4 SD 0.5	Med. 53 SD 14	Med. 0.03 SD 0.006	Med. 715 SD 216	Med. 843 SD 53	Med. 4 SD 1.3	Med. 34 SD 8
<b>ŚNP</b>								
<i>n</i> = 31	O	AM 11	AM 3,214	AM 0.17	AM 2,516	AM 1,143	AM 13	AM 98
		GM 10	GM 1,212	GM 0.14	GM 2,081	GM 1,080	GM 13	GM 91
		Med. 10 SD 5	Med. 2,452 SD 4,756	Med. 0.12 SD 0.105	Med. 2,747 SD 1,395	Med. 1,097 SD 390	Med. 12 SD 4	Med. 88 SD 40
<i>n</i> = 11	A	AM 12	AM 10,809	AM 0.21	AM 1,096	AM 524	AM 7	AM 65
		GM 10	GM 9,689	GM 0.17	GM 543	GM 415	GM 7	GM 60
		Med. 8 SD 8	Med. 8,600 SD 6,215	Med. 0.16 SD 0.163	Med. 353 SD 1,202	Med. 310 SD 431	Med. 6 SD 3	Med. 63 SD 27
<i>n</i> = 6	B	AM 7	AM 13,967	AM 0.06	AM 1,114	AM 133	AM 7	AM 43
		GM 5	GM 12,472	GM 0.05	GM 858	GM 126	GM 6	GM 38
		Med. 4.5 SD 6	Med. 11,550 SD 8,539	Med. 0.06 SD 0.037	Med. 660.5 SD 1,045	Med. 140 SD 46	Med. 6 SD 3	Med. 36 SD 28
<i>n</i> = 8	N1	AM 4	AM 64	AM 0.02	AM 847	AM 1,109	AM 3	AM 46
		GM 4	GM 61	GM 0.02	GM 831	GM 1,105	GM 3	GM 46
		Med. 3.5 SD 1	Med. 54.5 SD 21	Med. 0.02 SD 0.004	Med. 858 SD 174	Med. 1,111 SD 102	Med. 3 SD 0.8	Med. 43.5 SD 7
<i>n</i> = 8	N2	AM 3	AM 68	AM 0.03	AM 1,287	AM 1,088	AM 5	AM 54
		GM 3	GM 67	GM 0.03	GM 1,254	GM 1,087	GM 5	GM 53
		Med. 3 SD 0.5	Med. 63.5 SD 13	Med. 0.03 SD 0.005	Med. 1,259 SD 307	Med 1,096.5 SD 53	Med. 4.5 SD 2	Med. 52.5 SD 11
<b>MNP</b>								
<i>n</i> = 33	O	AM 15	AM 4,449	AM 0.19	AM 1,800	AM 1,236	AM 21	AM 89
		GM 14	GM 2,166	GM 0.16	GM 1,296	GM 1,210	GM 16	GM 77
		Med. 13 SD 6	Med. 4,051 SD 4,231	Med. 0.15 SD 0.105	Med. 1,595 SD 1,489	Med. 1,226 SD 249	Med. 15 SD 17	Med. 68 SD 73
<i>n</i> = 16	A	AM 27	AM 18,294	AM 0.19	AM 817	AM 478	AM 7	AM 75
		GM 17	GM 17,641	GM 0.17	GM 664	GM 445	GM 6	GM 66
		Med. 15 SD 44	Med. 16,450 SD 5,416	Med. 0.14 SD 0.115	Med. 927 SD 477	Med. 455 SD 197	Med. 4.5 SD 6	Med. 65 SD 53
<i>n</i> = 8	B	AM 24	AM 22,125	AM 0.08	AM 1,179	AM 231	AM 8	AM 66
		GM 17	GM 21,397	GM 0.07	GM 1,076	GM 221	GM 6	GM 60
		Med. 14 SD 30	Med. 20,300 SD 6,354	Med. 0.08 SD 0.028	Med. 1,164 SD 509	Med. 220 SD 74	Med. 4.5 SD 7	Med. 57 SD 38
<i>n</i> = 16	N1	AM 4	AM 78	AM 0.02	AM 567	AM 1,093	AM 4	AM 42
		GM 4	GM 77	GM 0.02	GM 481	GM 1,082	GM 4	GM 40
		Med. 3 SD 1	Med. 78 SD 17	Med. 0.02 SD 0.003	Med. 518.5 SD 317	Med. 1,049.5 SD 172	Med. 4 SD 2	Med. 40 SD 12

**Table 1** continued

Park	Medium	Cu (mg kg <sup>-1</sup> )	Fe (mg kg <sup>-1</sup> )	Hg (mg kg <sup>-1</sup> )	Mn (mg kg <sup>-1</sup> )	S (mg kg <sup>-1</sup> )	Sr (mg kg <sup>-1</sup> )	Zn (mg kg <sup>-1</sup> )
n = 16	N2	AM 3	AM 95	AM 0.04	AM 852	AM 1,062	AM 7	AM 48
		GM 3	GM 92	GM 0.04	GM 748	GM 1,049	GM 6	GM 46
		Med. 3	Med. 92.5	Med. 0.04	Med. 706	Med. 1,037	Med. 6	Med. 46
		SD 0.4	SD 23	SD 0.008	SD 479	SD 171	SD 3	SD 13

Explanation of symbols: O, A, B—organic, humic and illuvial soil horizons; N1—1 year old, i.e., 2001, Scots pine needles; N2—2 years old, i.e., 2000, Scots pine needles

AM arithmetic mean, GM geometric mean, Med. median, SD standard deviation, WNP Wigierski National Park, ŚNP Świętokrzyski National Park, MNP Magurski National Park

Silurian clayey shales, and greywacke covered by Pleistocene sands and tills, Lower Devonian quartzitic sandstones, siltstones, and clayey shales. The soils, corresponding to the geologic structure of the park, include rankers and acidic brown soils developed on sandstones, whereas gleyed acid brown soils, chernozems, and pseudogley lessives occur on tills (Migaszewski et al. 2004). The whole area of WNP is covered with Würm glaciation deposits (tills and fluvioglacial sands with cobbles and boulders) reaching 150 m in depth. The spectrum of soils developed on this allochthonous material includes rusty (arenosols) and podzolic soils (Migaszewski et al. 2005).

Chemical analyses were performed according to the methods and techniques used for environmental samples (soils and vegetation) in the Central Chemical Laboratory of the Polish Geological Institute in Warsaw. Of the more than 300 samples, 10% was randomly selected for routine replicate analyses, and international standards were inserted at a frequency of 5%. Analyses of soils were performed on the < 0.063 mm fraction, digested with aqua regia, and dissolved with concentrated hydrochloric acid. Plant samples were rinsed briefly three times with deionized water, and dried. Pulverized pine needle samples were digested with a mixture of concentrated nitric acid and deionized water (1:1) in a closed microwave system (MDS 81, CEM Corp., Matthews NC, USA). Analyses of element concentrations were conducted using inductively coupled plasma-atomic emission spectrometry (ICP-AES; spectrometer Jobin-Yvon model JY 70 PLUS with vertical plasma) and Hg was determined using an atomic absorption spectroscopic method (AAS; Altec amalgam analyzer AMA 254). Total sulfur was determined using a coulometric technique.

The iterative 2σ-technique is based on the assumption that all values beyond the mean ± 2σ are omitted until all the values lie within this range (approaching a normal distribution). The results of the general statis-

tics calculations for Cu, Fe, Hg, Mn, S, Sr, and Zn are presented in Tables 1 and 2. It should be emphasized that in some cases there are too few results (<10) to meet the assumption of minimum sample numbers; however, the author presents them for discussion purposes.

### Results and discussion

Both the summary statistics (Table 1) and calculated values (Table 2) show diversity among the three study areas, which confirms the dominance of local control of geochemical background values. Only Cu (10, 15, 17 mg kg<sup>-1</sup>) and S (1,486, 1,722, 1,613 mg kg<sup>-1</sup>) in the soil horizon-O, Cu (5, 6, 5 mg kg<sup>-1</sup>), Hg (0.03, 0.03, 0.03 mg kg<sup>-1</sup>), Sr (4, 4, 7 mg kg<sup>-1</sup>), Zn (51, 62, 59 mg kg<sup>-1</sup>) in the one-year pine needles, and Cu (5, 4, 3 mg kg<sup>-1</sup>), Hg (0.04, 0.04 mg kg<sup>-1</sup>) in the two-year-old pine needles are highlighted by similar background values (Table 2). Most of the results reflect an impact of anthropogenic pollution sources on the three parks examined. The highest background values of Cu and Fe were recorded in the soils of MNP. In contrast, the concentrations of Mn and Zn in the soils and pine needles of ŚNP reflect natural geogenic anomalies. Their distribution is in many cases nearly normal, which meant that no data were eliminated during calculations.

The background values of the soils reveal both areal and vertical diversity. In general, the concentrations of elements usually decrease with depth O > A > B. Fe tends to accumulate in the horizon-B in all national parks. The horizon-A of ŚNP and MNP shows the lowest background values for Mn and Sr, and the highest for Cu. Compared to the remaining horizons, the horizon-A of WNP is highlighted by the highest concentrations of Sr. In addition, the calculated background concentrations for the pine needles differ within the two age classes. The most distinct differences occur for Mn and S. The pine needles also

**Table 2** Upper limits of the mean  $\pm 2\sigma$  range and number of eliminated values to approach the normal range in the soils and Scots pine needles at Wigierski (WNP), Świętokrzyski (ŚNP) and Magurski (MNP) National Parks

Park	Medium	Cu (mg kg <sup>-1</sup> )	Fe (mg kg <sup>-1</sup> )	Hg (mg kg <sup>-1</sup> )	Mn (mg kg <sup>-1</sup> )	S (mg kg <sup>-1</sup> )	Sr (mg kg <sup>-1</sup> )	Zn (mg kg <sup>-1</sup> )
WNP <i>n</i> = 22	O	10 -1 value	2,694 -3 values	0.18 -1 value	1,158 -5 values	1,486 -1 value	18 -3 values	58 -4 values
ŚNP <i>n</i> = 31	O	15 -3 values	4,098 -5 values	0.38 -0 values	5,043 -1 value	1,722 -2 values	21 -2 values	143 -3 values
MNP <i>n</i> = 33	O	17 -9 values	10,640 -3 values	0.27 -4 values	4,778 -0 values	1,613 -3 values	30 -4 values	90 -6 values
WNP <i>n</i> = 12	A	4 -3 values	8,310 -2 values	0.08 -1 value	1,078 -1 value	340 -2 values	38 -1 value	31 -2 values
ŚNP <i>n</i> = 11	A	20 -1 value	12,694 -2 values	0.37 -1 value	2,604 -1 value	390 -4 values	8 -2 values	120 -0 values
MNP <i>n</i> = 16	A	24 -2 values	21,441 -3 values	0.27 -2 values	1,576 -1 value	630 -2 values	6 -5 values	91 -1 value
WNP <i>n</i> = 7	B	4 -1 value	9,999 -1 value	0.02 -1 value	786 -0 values	132 -0 values	5 -1 value	23 -1 value
ŚNP <i>n</i> = 6	B	6 -1 value	31,045 -0 values	0.13 -0 values	3,205 -0 values	225 -0 values	13 -0 values	100 -0 values
MNP <i>n</i> = 8	B	22 -1 value	34,832 -0 values	0.13 -0 values	2,197 -0 values	378 -0 values	22 -0 values	77 -1 value
WNP <i>n</i> = 15	N1	5 -4 values	52 -4 values	0.03 -0 values	817 -0 values	1,002 -1 value	4 -4 values	51 -0 values
ŚNP <i>n</i> = 8	N1	6 -1 value	85 -1 value	0.03 -0 values	1,194 -0 values	1,314 -0 values	4 -0 values	62 -0 values
MNP <i>n</i> = 16	N1	5 -1 value	113 -0 values	0.03 -1 wart	895 -2 values	1,116 -4 values	7 -1 value	59 -1 value
WNP <i>n</i> = 15	N2	5 -0 values	57 -4 values	0.04 -1 value	951 -2 values	910 -2 values	6 -1 value	50 -0 values
ŚNP <i>n</i> = 8	N2	4 -1 value	95 -0 values	0.04 -0 values	1,901 -0 values	1,194 -0 values	5 -1 value	75 -0 values
MNP <i>n</i> = 16	N2	3 -2 values	132 -1 value	0.05 -3 values	1,117 -3 values	1,306 -1 value	14 -0 values	74 -0 values

reveal a spatial element distribution, which is highlighted especially by Fe (background values: 52, 85, 113 mg kg<sup>-1</sup> for the one-year-old pine needles and 57, 95, 132 mg kg<sup>-1</sup> for the two-year-old ones).

The calculated background values are higher than medians or means of the original data. Therefore, the ecosystems of this study belong to relatively “clean” areas. The presented background values seem to be realistic on a local scale and may serve for establishing environmental quality standards, as well as for assessing an impact of anthropogenic pollution sources, together with other supplementary investigations, such as sulfur stable isotope determinations and scanning electron microscope study of airborne particulates.

## Conclusions

The discussion of the use of the term “geochemical background” and the results of integrated geochemical background values, calculated for soils and Scots pine

needles of the three selected national parks lead to the following conclusions:

1. There is a strong need for providing a precise definition and feasible methods for determining geochemical background in different environmental samples. Since the background value for a given substance is theoretical, different methods of assessing it, i.e., geochemical, statistical, and integrated, may be used. In order to avoid confusion, only some of these methods should be officially suggested for different purposes, including exploration and environmental geochemistry.
2. The background values are different for remote areas, and are governed primarily by the geologic setting of the region. This supports the view on the restricted extent of geochemical background. The data indicate that it may be assessed only on a local or regional scale at the most.
3. The present study shows that the background values vary with depth of the soil profile and within

pine needles of different age classes. This indicates that, when conducting geochemical and biogeochemical investigations in forest ecosystems, samples should be collected from the same soil horizon, plant species, and plant organs etc.

4. Calculation of geochemical background requires using the same methods of sampling, sample preparation (e.g., screening, digestion), and element or organic compound determinations. In addition, all the environmental and biological factors should also be taken into consideration in order to avoid any interpretative pitfalls. The more multifaceted the approach is to a given statistical method, the better the chances are for obtaining reliable results.

The use of the integrated method in geochemical and biogeochemical studies in relatively pristine areas seems to be a good way of calculating these idealized background values. However, the observed and 95% expected baselines will still be competing with the background, especially in unpolluted natural ecosystems.

**Acknowledgments** The author thanks Dr. Zdzislaw M. Migaszewski of the Pedagogical University in Kielce for encouraging me to write this paper, allowing me to use the archival data, and making comments on the subject discussed that certainly influenced the quality of my paper. I would also like to express my gratitude to Dr. Larry P. Gough of the US Geological Survey in Reston, Virginia for reading the final version of my paper and for the valuable remarks.

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