Geochemical background – can we calculate it?

J. Matschullat · R. Ottenstein · C. Reimann

Abstract The term "background" is discussed and a definition is suggested to put an end to the currently unsatisfying (non-)definition of *geochemical* or *natural background*. Based on the requirements stated in the definition, several simple and robust statistical methods are applied to different data sets ($n>50$) from the atmosphere, pedosphere, and biosphere in order to explore their potential for the evaluation of a useful and robust background. Compared with the original data set both the calculated distribution, based upon the lower 50% of the values, as well as a 2σ-approximation of the normalised data set lead to promising and realistic results. Both methods seem appropriate for a fast and reliable evaluation of likely upper limits of background values. Nevertheless, even this robust method is not able to present absolute and doubtlessly correct background values. True quantification of any natural or geochemical background still requires a thorough investigation and is impossible without costly expert knowledge.

Key words Background · Data distribution · Normal distribution · Log-normal distribution · Geochemistry · Environmental science · Robust geostatistics

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Introduction

The term "geochemical background" became an important reference with increasing environmental awareness and with a rising number of pollutant investigations into air, water, soil, and sediment. There is also practical relevance in defining the borderline between concentrations of a chemical element or component that naturally occurs in these media as compared with the concentrations of the same analytes present as a result of anthropogenic activities. We presume, however, that the communicating partners agree about the meaning of the term and perhaps even its expression in numbers.

A literature search with the term background quickly yields an almost innumerable amount of citations. This shows that there is obviously a demand for the term. A closer inspection of its use reveals, however, that there seems to be no clear definition or agreement on its use. The agreement is, in most cases, inherently assumed and the term is used rather imprecisely – often in the sense of "threshold value". Since the meaning of "geochemical background" is crucial and important, whenever natural or geogenic influences are to be separated from non-natural or anthropogenic influences, it is correct to put some effort both into a clear and unmistakable definition and into the necessary methods to obtain the respective information.

The following citations exemplify how imprecise the definition of a geochemical background seems to be and thus at least partly explain the related misunderstandings:

"Background concentration of pollutants. If the atmosphere in a particular area is polluted by some substance from a particular local source, then the background level of pollution is that concentration which would exist without the local source being present. Measurements would then be required to detect how much pollution the local source is responsible for" (Porteous 1996).

"*Background concentration: the natural base load*" (Pfannkuch 1990).

From a geochemical point of view, the term background is equivalent with the absence of an anomaly. The term was coined by exploration geochemists in order to differentiate between the element (or compound) concentration within a rock matrix devoid of enrichments and those rock parts that show positive anomalies. Therefore, background concentrations are not necessarily equal to low concentrations. In any case, concentrations will have to be quantified to be used as a reference. This quantification requires a thorough and critical quality control of the data. The importance of this quality control becomes apparent when scrutinising the literature: Bowen (1979) compiled global data for relevant environmental compartments which are still being used as a reference. When these data are compared with results from much more recent works, mainly in respect to trace element concentrations in waters and in the atmosphere, partly also in soils and sediments, it becomes apparent that much lower concentrations are published today (e.g. Bruland 1983; Reimann and Caritat 1998; Salbu and Steinnes 1995). This presumed decline of background concentrations can almost exclusively be explained by a growing awareness in the scientific community with respect to much more thorough sampling and analytical techniques. In the past, contamination problems and artefacts have not been given the appropriate attention by the majority of workers (see Gasparon 1998; Naumann 1996; Patterson and Settle 1976; Zhang and others 1995).

At the same time, it is crucial to acknowledge the natural variability of any analyte in a given matrix under the aspect of the migration of chemical compounds and elements within and between individual environmental compartments. Considering the variables (element occurrence in minerals, migration, geochemical gradients and fluxes, geochemical barriers, etc.), it becomes obvious that reliable data of limited variance exist for certain lithologies, but that the idea of a “global”, in the sense of generally valid, geochemical background, e.g., for soils and sediments, must remain an illusion (e.g. Reimann and Filzmoser 1999; Steiger and others 1996). A geochemical background is characterised by regional variability and it is a function of time. This is increasingly being recognised by the scientific community – although there is still no satisfying definition available. Prior to a definition, there will have to be an agreement about the general difference between the above-mentioned background for lithologies and a background for smaller geological bodies like soils and sediments, including waters and the composition of the atmosphere in respect to trace and ultra-trace compounds. Thus, a definition has to follow primarily practical and user-related criteria.

Definition

The geochemical or natural background is a relative measure to distinguish between natural element or compound concentrations and anthropogenically-influenced concentrations in real sample collectives. This distinction mainly aims at an unmistakable characterisation and quantification of the concentration range of an analyte in anthropogenically non-influenced samples. Such a differentiation is only useful in samples with elevated analyte concentrations which may, by themselves or in combination with other compounds, lead to a limitation of the usage potential of the investigated medium for humans, animals or plants in respect to health constraints.

Assumptions

- The determination of a geochemical background requires the ability to sample, work and quantitatively analyse the medium of interest without losses or contamination of the analyte.
- Because of the extreme variability of analytes within the individual environmental spheres and compartments, a geochemical background can only be derived for a defined spatial setting. This determination requires the proof of relative homogeneity and thus comparability of the investigated matrix within the investigated space. This homogeneity is identical with a certain similarity mainly of climatological, lithological and pedological characteristics.
- Naturally- and anthropogenically-induced processes not only lead to a widening of the range of the data collective (larger standard deviations), but also to multi-modal distributions. Ideally, each mode corresponds to a relevant process with its underlying normal distribution. Since the anthropogenic influence occurs by definition only as a contamination in the sense of a positive anomaly, the search for the geochemical background is reduced to the recognition of the relevant data sub-collective and its quantitative description.
- The citation of single values for a geochemical background is neither useful for the characterisation of the geogenic background nor for the determination of an anthropogenic contamination, because single values do not yield information about the natural deviation. Consequently a differentiated interpretation of results would be impossible. It is possible, however, to define upper limits for the background with a defined statistical reliability.

This contribution discusses the topic from a conceptual point of view. The intent is both to increase awareness for the necessity of an unmistakable definition and at the same time to demonstrate with real samples the problem of the practical differentiation between naturally- (geogenic) and anthropogenically-influenced element concentrations. The authors believe that it is in principle almost impossible to quantify a true background value beyond doubt. It seems possible, however, to derive a plausible and more realistic approximation for background values.

Methods to calculate the background

In general, a distinction between geochemical and statistical methods can be made. The global marine “shale standard” after Turekian and Wedepohl (1961), or any of the upper crust averages, as well as all works that refer to precivilizatorical accumulations and formations on a local or regional scale are part of the geochemical methods (archives such as limnic and marine sediments, overbank and river sediments, cave sediments, etc.). These approaches can be seen as an attempt to interpret individual samples or sampling profiles (including bore holes) and to select representative samples for a given target area. Additional parameters like pH-values, C- and S-content, and isotope data are usually needed for the interpretation. From these, the geogenic background is determined, mainly as a fixed value (mean or median). This determination requires expert knowledge about the geochemical behaviour of the investigated elements under the prevailing environmental conditions, including paleoenvironmental conditions. No information is needed in respect to the distribution function. The determined values thus represent hypothetical baseline concentrations without consideration of the natural variability. These methods can be addressed as empirical. They depend upon expert knowledge and are not free from bias (subjective decision criteria). This approach is not being followed further in this paper.

The other approach uses statistics. It should be pointed out, however, that the data often do not comply with the formal requirements of parametric statistics, but need non-parametric methods, just like most data from the life sciences. This requirement seems to contrast with the above-stated assumption that the natural element distribution may be described via a normal or log-normal distribution (Reimann and Filzmoser 2000). An approximation to a solution for this problem may be seen in the assumption that each of the processes involved in the generation of the data will in itself produce a data set showing a more or less normal distribution, and that the number “*n*” of the processes will largely overlap. With the above-stated definition in mind, positive anomalies will have to be detected and eliminated as fingerprints for processes “disturbing” the normal data distribution. These deviations can be interpreted as anthropogenic influences that overlap the natural data distribution mostly through skewed enrichments. Most statistical tests are only helpful in eliminating so-called outliers, and thus to reduce the original data set to a “clean” data collective. From this reduced data set, which is being addressed as *anthropogenically undisturbed*, the essential descriptive statistical parameters can be calculated. The sole communication of any mean value without its standard deviation (σ) is of little use, and may only be used in comparison with geochemical methods. It makes sense, however, to show concentration ranges (e.g. the normal range of a sample as defined by the $\text{mean}\pm 2\sigma$; this means that ca. 95% of the samples come within this range) or upper values (threshold level; e.g., $\text{mean}+2\sigma$, which means that ca. 97% of the samples lie below this value). Only this type of data includes sufficient information about the natural scatter of the background (including scatter through experimental set up). Even here, a bias through the necessary inclusion of expert knowledge cannot be ruled out, since the influence of natural processes will have to be assessed realistically. The following examples for the tested methods have been performed with the same original data set (drill cores from overbank sediments of the Havel river, a tributary to the Elbe river).

No concession has been made to methods that include problems, e.g. of synsedimentary but granulometrically different sediment facies (e.g. Hanson and others 1993).

Lepeltier method

Lepeltier (1969) suggested a method with a graphical evaluation of cumulative sums in double-logarithmic scale graphs. The method was developed for ore prospecting but is applicable to determine the geogenic background because it is the aim of prospecting to detect positive geochemical anomalies. Only the average element concentration (Clarke-value) is required. Lepeltier’s ideas are based upon the assumption that trace element values show a log-normal distribution. By drawing the relative cumulative frequencies in a logarithmic scale (sum backwards), a deviation from log-normal distribution can easily be seen as a bend in the curve. The background is then given as the mean of the undisturbed distribution function and the calculated “threshold-level” ($=\text{mean}+2\sigma$). This method is presented in a slightly modified form in Fig. 1. The bend (arrow, distinct alteration of the slope) cuts the data set in two parts. From the complete data set the descriptive statistical values can be derived graphically (as by Lepeltier), or calculated for the part with low frequencies. The other sub-collective (here >30 mg kg^{-1}) can be seen as an anomaly and will no longer be considered for the geogenic background. It becomes obvious that this method cannot be applied to small data sets since there will be too few data in order to unmistakably describe a bend in the curve.

Relative cumulative frequency curves

In close approximation to the Lepeltier method, this technique requires curves of the individual elements to display the relative cumulative frequency linearly. Bauer and Bor (1993, 1995) and Bauer and others (1992) define the first bend of the slope in the curve as the upper limit of any background data collective (here >30 mg kg^{-1}). A bend in the upper part of the graph (high values) can be used to distinguish between anthropogenically non-influenced samples (comparatively low values, large scatter) and anthropogenically-influenced samples (high concen-

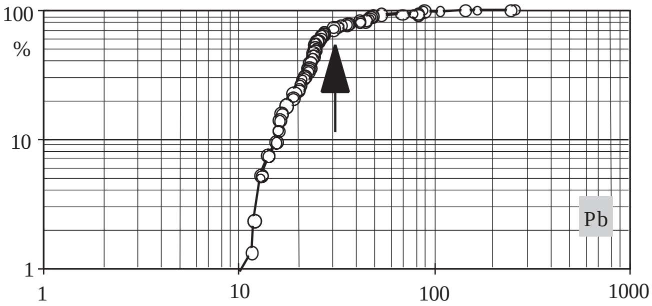

Fig. 1
Example illustrating the Lepeltier method. Concentration (mg kg^{-1}) is plotted against the relative cumulative frequencies. The *arrow* points at the turning point that separates two data subsets

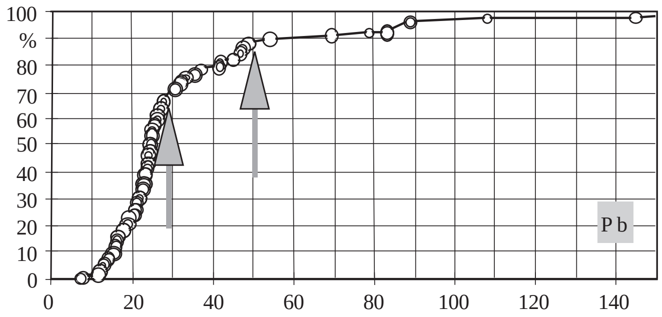

Fig. 2
Example for relative cumulative frequency curves. The two *arrows* point at two turning points that separate the "background" values (0–70%), from samples which may not be influenced by human impacts (70–90%), and anthropogenically influenced samples (>90– 100%)

trations, large scatter). This technique does not require any assumption concerning the distribution function. The example in Fig. 2 shows that the bend may be even more difficult to allocate as compared with the Lepeltier method (arrows). This is due to the chosen scale (axis are elongated as compared to the logarithmic display), but may be an advantage with further data interpretation. Several bends may hint at either a multitude of interfering processes or point to a data set which is not compatible with the applied technique.

Normal range of a sample

Also related to the Lepeltier method is an approach by Hindel and Fleige (1991) that defines the 97.5-percentile of anthropogenically non-influenced samples as the upper limit of the background. This approach seems to be problematic since no criterion exists that allows one to distinguish a priori between contaminated and non-contaminated samples. The definition of the background as "the normal range of a sample" (mean $\pm 2\sigma$) requests the assumption of a log-normal distribution. To demonstrate its applicability, only "anthropogenically-undisturbed samples" were used by the authors. In the example of a soil investigation, the distinction was made as follows (simplified): the element concentrations in the fraction >2 mm were compared with the fraction <2 mm. If the quotient was close to or smaller than one, then the sample was addressed as being "anthropogenically undisturbed" (valid for soils from rock weathering and younger sediments). The determination of the background (mean $+2\sigma$) is then done either graphically (plotting of the relative cumulative frequency in a logarithmic scale, "sum backwards", and reading of the upper limit at the 97.5-percentile) or by calculation (the standard deviation of the log-transformed data).

Regression-technique

The measured element concentrations have to be fitted with one or several conservative elements that are not influenced by anthropogenic activities (e.g. Al, Zr, etc.). This is done by linear regression so that the background can be calculated for every single point that confirms with the regression conditions. Samples that lie beyond the confidence interval (95%) will be posted as "anthropogenically influenced". This technique has been used by Bauer and Bor (1993, 1995) and Bauer and others 1992.

Mode-Analysis

A method propagated by Graf and Henning 1952. The objective of this method is the separation of multi-mode distribution functions into several normal distributions, the means of which correspond with the respective (relative) mode values of the initial distribution function (Carral and others 1995). In this example, the original data are first normalised using the samples Al-concentrations and then subjected to the mode analysis. The background is derived as the upper limit of the 95%-confidence interval of the mean from the normal distribution of the lowest mean value (1). The result of such a mode analysis is being demonstrated in a modified form (no normalisation was done with another element) in Fig. 3. The numbers indicate the mode values of the derived sub collectives, The width of the respective distribution function increases from (1) to (4).

4σ-outlier test

Assuming a normal distribution of trace elements in samples, and using an appropriate data set ($10 < n < 1000$), an outlier test using the 4σ-criterion can be applied (If there are more than ten values, an individual value can be interpreted as an outlier if it is further from the mean than 4σ). This requires the elimination of potential outliers (e.g., from the cumulative relative frequency curves) from the data set and the calculation of the mean and the standard deviation for the remaining sub-collective. Previously "emotionally defined" outliers can be classified objectively with this method. The resulting sub-collective (free from outliers which can be interpreted as anthropogenically-influenced samples or anomalies) is defined as reflecting geogenic or background conditions. The resulting mean $\pm 2\sigma$ will be seen as the

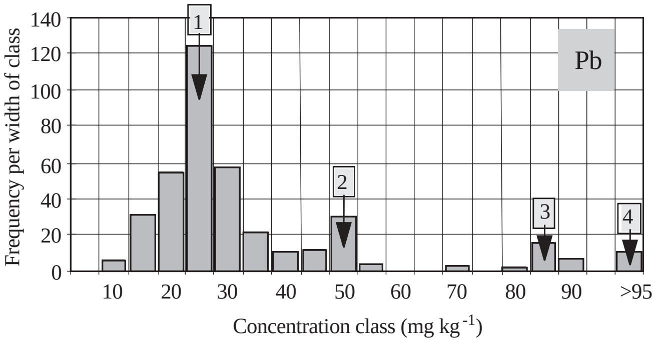

Fig. 3
Example for the mode analysis. Four modes occur in the given example: (1) stands for the mode of the background subcollective, (2) for additional subcollectives which stand each for individual processes that lead to the distinctive data distribution

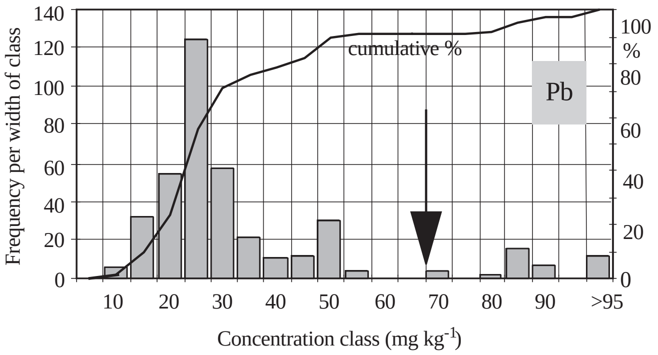

Fig. 4
Example for the 4σ-criterion Outlier test. The *arrow* represents the upper concentration limit for the background subcollective as defined by this test

normal range for the background. Figure 4 displays this upper limit (arrow: ca. 70 mg kg^{-1}). The resulting median value of the corresponding distribution function will fall into the class with the highest frequency.

Iterative 2σ-technique

Comparable with the outlier test, but more radical and mathematically less robust, this technique aims at defining the background by approaching a normal range (Erhardt and others 1998). Mean and standard deviation are calculated for the original data set. All values beyond the mean ± 2σ interval are omitted. This procedure is repeated until all remaining values lie within this range. The mean ± 2σ calculated from the resulting sub-collective is considered to reflect the geogenic background. This technique constructs an approximated normal distribution around the mode value of the original data set. The result is not necessarily identical with that of a mode analysis, since there, the lowest relative mode value is obtained, while this technique is more likely to refer to the mode value of the original distribution). The upper limit of the 2σ-range of the data set for the previous examples is displayed in Fig. 5 (arrow: ca. 30 mg kg^{-1}). The mean (median) of the related distribution again lies in the class with the highest frequency. Since this technique does not consider the other hypothetical distribution functions (with respect to higher values) like the 4σ-outlier test, the upper limit is consequently considerably lower.

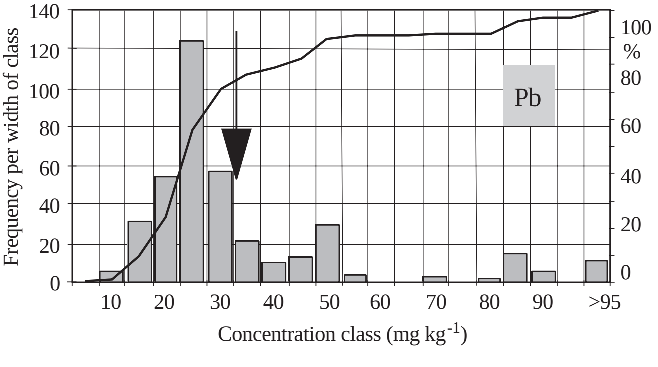

Fig. 5
Example for the iterative 2σ-method. The *bars* show the histogram in the given concentration intervals; the *line* represents the cumulative frequency curve (see also Fig. 4), and the *arrow* points at the upper limit of the 2σ-derived background subcolective

Calculated distribution function

Enrichments and depletions balance out in natural processes. An enrichment in a certain layer or compartment will be related to a depletion in another compartment or layer over a longer period of time. Anthropogenic influences tend to lead to enrichments in individual compartments or parts of natural systems – the distribution function will be disturbed one-sided towards higher values (skew). The lower values should therefore be free from anthropogenic influences (this of course is only partly true, because any kind of anthropogenically induced depletion, e.g. via acidification processes in soils and sediments are being neglected here). From the minimal value to the median value (which is inherently stable against outliers and deviations) the data set should most likely represent natural processes and thus the natural background (= reduced data set). Under this premise, a "natural" non-anthropogenically influenced distribution function can be constructed. To do this, every single value of the reduced data set is being "mirrored" against the original median value by adding the distance from the individual value to the median to obtain a new value larger than the median (= calculated distribution function). For this function the relevant descriptive statistical base parameters are calculated and the mean ± 2σ is then again seen as the normal range of the geogenic background. The results for the exemplifying data set are given in Figs. 6 and 7 (upper limit: mean + 2σ; arrow in Fig. 7: ca. 40 mg kg^{-1}).

There are two major requirements that any statistical method aiming at the determination of a geogenic background will have to fulfil: robustness and a broad applicability. This means that the chosen algorithm has to be equally reliable with any data set of any given medium.

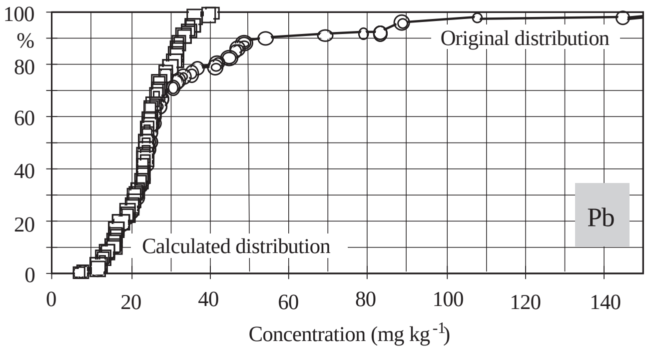

Fig. 6
Example for the calculated distribution function. The two *lines* represent both the original (*open circles*) and the calculated distribution (*open squares*)

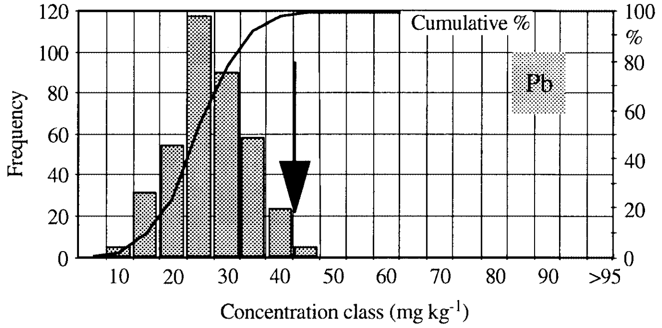

Fig. 7
Example for the frequency distribution of the calculated distribution function with upper threshold: mean + 2σ (*arrow*)

To test these requirements, the following section uses the iterative 2σ-technique, the 4σ-outlier test and the calculated distribution function on several independent data sets.

Application examples

The following examples refer to data sets which have been influenced by anthropogenic activities (dry atmospheric deposition, lichens, mosses and humic topsoil) and others that were predominantly influenced by natural element dispersion and accumulation processes (B- and C-soil horizon). In all six data sets, elements were selected for both their natural or anthropogenic signatures. All data sets have been thoroughly tested for accuracy and completeness. The data themselves have been published and interpreted (mosses and humic topsoil, B- and C-horizon: Reimann and others 1998; dry atmospheric deposition: Kritzer 1995; lichens: Matschullat and others 1998). The most plausible calculation of the geogenic background was tested using statistical techniques. All of the following tables show an identical layout for ease of comparison and display the mean and median values of the original data set, the results from the fitted distribution (2σ), the 4σ-outlier test, and the calculated distribution. In addition, the relative standard deviation (σ) is given, the number "n" of single values within the collective/sub-collective, and the relative loss of individual data points after the respective fitting (data representation). The latter, however, is not being displayed with the calculated distribution. Finally the calculated upper limit (mean + 2σ; rounded) of the natural background is given. Figure 8 sums up the obtained results (calculation of the upper limit of a calculated background for the data from the Kola peninsula).

Atmospheric dry deposition in the eastern Erzgebirge

Data are based upon two atmospheric observation stations where dry deposition was sampled from May 1992

Fig. 8
Comparison of the results of the three statistical tests for the evaluation of a natural background, performed with data from the Kola-project media "moss", "humic topsoil", "B-horizon", and "C-horizon". It becomes obvious that the results obtained from the applied statistical tests stay reasonably close (except for the 4σ-test Ni in Moss)

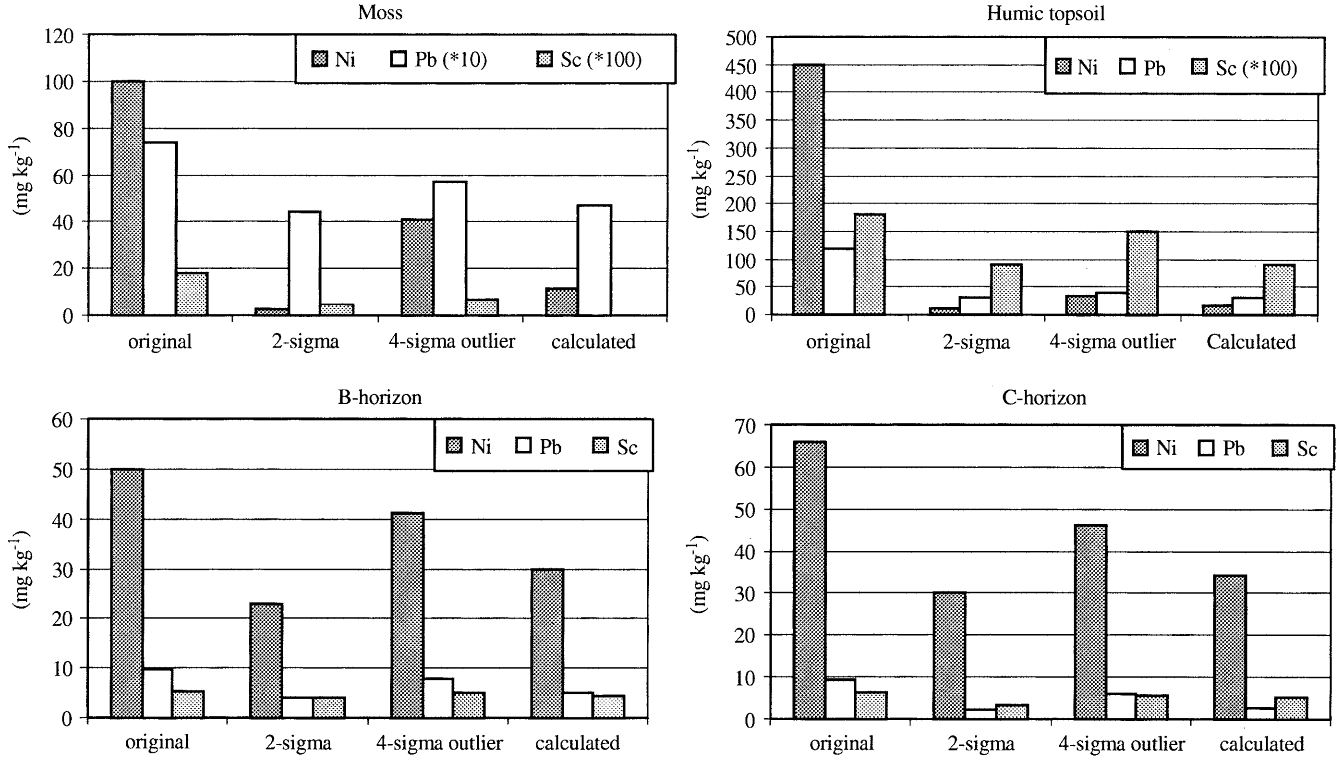

Table 1
Statistical parameters for the aerosol data set (ng m^{-3}) from the eastern Erzgebirge, and their alteration through three statistical tests to derive a natural background (see text)

	K	Ni	Pb	
Mean	306	7.2	35.7	
Median	242	3.0	22.7	Original data set
σ [%]	76	315	92	
Number *n*	111	111	111	
Upper limit 2σ	770	50	100	
	K	Ni	Pb	
Mean	197	1.8	17.5	
Median	191	1.5	16.3	2σ-method
σ [%]	40	58	46	
Number *n*	80	70	77	
Loss [%]	28	37	31	
Upper limit 2σ	350	4	34	
	K	Ni	Pb	
Mean	286	3.8	35.7	
Median	240	3.0	22.7	4σ-outlier test
σ [%]	60	91	92	
Number *n*	109	107	111	
Loss [%]	2	4	0	
Upper limit 2σ	630	11	100	
	K	Ni	Pb	
Mean	242	3.0	22.7	
Median	242	3.0	22.7	Calculated distribution
σ [%]	41	58	47	
Upper limit 2σ	440	6.5	44	

to April 1994 using Low Volume Samplers. The filters were analysed directly with PIXE and neutron activation, and with GF-AAS after total digestion. The elements were chosen to represent strongly anthropogenic signatures (Pb), a dominantly geogenic component (K) and an intermediate element with both geogenic and anthropogenic influences (Ni) (Table 1; Kritzer 1995; Matschullat and Kritzer 1997).

The original data set shows a skewed distribution with a distinct difference between mean and median values. All techniques lead to a better approximation of these two values except for the 4σ-outlier test. The lowest standard deviations occur with the calculated distribution and with the 2σ-technique. In the 4σ-outlier test, the variance is visibly homogenised compared to the original data. This is particularly apparent for the example Ni. The 4σ-outlier test eliminates the lowest number of samples while 68% of all values remain in the application of the 2σ-technique. The calculation of an upper limit of a postulated geogenic background (defined as a positive 2σ-variance) leads to a distinct decline for Ni as compared to the original data set. This is only partly true for Pb and K, where solely the 2σ-technique and the calculated distribution yield significantly lower values.

The geogenic variation of K is very high; a relevant anthropogenic influence could be determined indirectly only as a higher K-deposition in rural regions resulting from mechanical soil disturbance and atmospheric K transport via soil dusts (Kritzer 1995). The element Ni is more likely to be influenced by anthropogenic processes. Reimann and Caritat (1998) describe maximum air concentrations in remote areas of 3.2 ng m^{-3}. This number comes close to the result of the 2σ-technique, while both of the other two tests yield considerably higher values. For Pb, Reimann and Caritat (1998) cite an upper limit of 21 ng m^{-3} – again a decent approximation obtained with the 2σ-technique and with the calculated distribution. Accepting a "safety factor" of 2, all results from the tests may be accepted as a decent approximation to the natural background.

Lichens as retrospective deposition monitors

In the summer of 1996, epilithic lichens were sampled at 25 localities within the Rhine-Neckar region, Germany. Most lichens live almost exclusively from atmospheric deposition and are thus appropriate biomonitors for air quality (e.g. Kirschbaum and Wirth 1997). The samples were investigated after HNO_3-digestion with ICP-MS and AAS-techniques. The elements Cr, Pb, and Rb were selected. Rubidium is representative for an anthropogenically less relevant element, Pb again for a dominantly anthropogenically released element, and Cr has an intermediate position (Table 2; Matschullat and others 1998).

The data set for epilithic lichens in the Rhine-Neckar region is relatively small. It can thus be taken as an example for a large number of real world data that are being gathered in environmental studies and where financial restrictions (or well thought out sampling strategies) restrict the total number of samples accordingly. Compared with data from the literature – here, maximum concentrations for terrestrial mosses in remote areas of Norway (cited in Reimann and Caritat 1998) – the obtained background values are quite similar: moss 30 mg Cr kg^{-1}, 79 mg Pb kg^{-1} and 62 mg Rb kg^{-1}. For the same lichen species (*Lecanora muralis*), Matschullat and others (1998) published an empirical background value of 16 mg Cr kg^{-1}, 18 mg Pb kg^{-1} and 3.4 mg Rb kg^{-1} for all of Germany. This contrasts with calculated upper limits of the background in the lichen data set: Cr ca. 33, Pb ca. 100, and Rb ca. 40 mg kg^{-1}. The difference between the original data set and the test results is only significant for the element Pb, while the Cr and Rb concentrations do not vary in a meaningful manner. Even if there is a limited comparability between element concentrations in lichens and mosses (there is a lack of independent data on epilithic lichens), the obtained values point in an appropriate direction. In all cases the tests lead to a clear distinction of the postulated background in relation to the original data set (for Germany) and its maximum values: Cr 167, Pb 1860, and Rb 94 mg kg^{-1}. Using the calculated upper limits of the background, this can be translated into anthropogenic contributions of 80% Cr, 95% Pb and 60% Rb. These amounts are quite realistic for Cr and Pb

Table 2
Statistical parameters of the original data set of epilithic lichens (mg kg^{-1}) from the Rhine-Neckar-area and their alteration through the application of three statistical methods to derive a natural background (see text)

	Cr	Pb	Rb	
Mean	20.4	88.6	26.5	Original data set
Median	19.8	76.3	24.1	
σ [%]	35	59	46	
Number *n*	50	50	50	
Upper limit 2σ	35	190	50	

	Cr	Pb	Rb	
Mean	19.6	71.7	24.5	2σ-method
Median	19.7	71.7	23.4	
σ [%]	33	19	30	
n	48	44	48	
Loss [%]	4	12	4	
Upper limit 2σ	33	200	40	

	Cr	Pb	Rb	
Mean	20.4	71.7	24.5	4σ-outlier test
Median	19.8	71.7	23.4	
σ [%]	35	19	30	
n	50	44	48	
Loss [%]	0	12	4	
Upper limit 2σ	35	100	40	

	Cr	Pb	Rb	
Mean	19.8	76.3	24.1	Calculated distribution
Median	19.8	76.3	24.1	
σ [%]	32	23	28	
Upper limit 2σ	33	110	38	

(Matschullat 1997), but appear too high for Rb. Since this phenomenon with unusual Rb-enrichments has also been observed by other authors (Jayasekera and Rossbach, FZ Jülich, oral comm. 1999), additional investigations on the role of the alkaline element Rb are needed.

Mosses and humic topsoil as retrospective deposition monitors

Almost 600 terrestrial mosses (*Hylocomium splendens* and *Pleurozium schreberi*) and 617 samples of humic topsoil were collected in the summer of 1995 on the Kola peninsula. The element concentrations were obtained through ICP-MS after HNO_3-digestion. Nickel is emitted in this area by point sources – the industrial centres of Monchegorsk, Nikel and Zapoljarnij. Lead (Pb), however, is being distributed in this area to a much smaller extent than compared to central Europe. The element Sc occurs in small and very small concentrations only, geogenic sources clearly prevail. In the mosses, most of the Sc-values are below the determination limit (Table 3; Reimann and others 1998).

Even with the mosses, a comparison of the obtained results with those of mosses from other regions is not beyond doubt. Although many mosses live almost exclusively through an atmospheric nutrient uptake, there is a lack of experience in respect to a reliable background for these organisms. Maximum values from Germany cited by Reimann and Caritat (1998) with Ni 16, Pb 144 and Sc 2,3 mg kg^{-1} partly deviate highly from the obtained results of the calculated background in this work. For Sc, a calculation is inapplicable due to many values below the determination limit. The calculated Ni background concentrations are estimated suspiciously low with the 2σ-technique. The value of 2.7 mg kg^{-1} is strikingly different from the results of the other two tests and appears to be unrealistically low. The calculated upper limits for Pb are in very good agreement. The above cited Pb-values from the literature are definitely rather high – in Germany Pb contamination is considerably higher than on the Kola peninsula. Compared with a maximum value of 29.4 mg kg^{-1} on Kola, values around 5 mg kg^{-1} can be seen as realistic for the background. This supports the postulated importance of a determination of local and regional background values, respectively. The local importance of Ni contamination (mainly through ore smelters and dressers) becomes just as apparent as the relatively low anthropogenic Pb contamination in the area.

Reimann and Caritat (1998) cite element concentrations in humic topsoil from forested areas in Norway with median values of 3.2 mg Ni kg^{-1}, 32.8 mg Pb kg^{-1} and 0.5 mg Sc kg^{-1}. The Kola data set shows much higher Ni concentrations, lower Pb concentrations, but almost identical Sc concentrations. After recalculation of the data sets, these published values fit relatively well with the limits for the geogenic background calculated in this work. Not plausible however, are the results of the 4σ-outlier test for Ni and Sc. The results of the Ni and Pb background calculation via the 2σ-technique and the calculated distribution are clearly different from the original data set and make a realistic impression.

B- and C-horizon of sub-arctic soils

A total of 578 soil samples from the B horizon and 605 samples from the C horizon were collected in the summer of 1995 on the Kola peninsula and analysed by ICP-OES after aqua regia extraction. The authors wish to point out that they are fully aware of the analytical limits of this extraction method when a quantification of absolute element concentrations is needed. Aqua regia extraction leads to negative errors and badly reproducible results (element dependent). This has no significance, however, for the topic of this paper (Table 4; Reimann and others 1998).

The element concentrations in both soil horizons correspond well. The calculated upper limits of the background differ mainly between test and original data in respect to the 2σ-technique and the calculated distribution. Reimann and Caritat (1998) cite forest soil B-horizons of Norway with median values of 8.5 mg Ni kg^{-1}; 13.4 mg Pb kg^{-1} and 3.3 mg Sc kg^{-1}. In respect to Ni, this is much lower than the calculated values of the Kola data set. The Pb values from Kola are much lower in comparison with

Table 3
Statistical parameters of the original data set of mosses and humic topsoil from the Kola peninsula (mg kg^{-1}), and their alteration through the application of three statistical methods to derive a natural background (see text)

	moss			humus			
	Ni	Pb	Sc	Ni	Pb	Sc	
Mean	19.5	3.3	0.06	51.0	24.1	0.69	
Median	5.4	3.0	0.05	9.2	18.8	0.50	Original data set
σ [%]	209	62	98	391	202	80	
Number "*n*"	598	598	598	617	617	617	
Upper limit 2σ	100	7.4	0.18	450	120	1.8	
	Ni	Pb	Sc	Ni	Pb	Sc	
Mean	1.9	2.8	0.05	5.6	17.3	0.48	
Median	1.8	2.7	0.05	5.5	17.0	0.50	2σ-method
σ [%]	21	28	0	38	28	44	
n	187	498	543	322	481	498	
Loss [%]	69	17	9	48	22	19	
Upper limit 2σ	2.7	4.4	0.05	10	30	0.90	
	Ni	Pb	Sc	Ni	Pb	Sc	
Mean	11.5	3.2	0.05	12.4	21.0	0.65	
Median	4.9	3.0	0.05	7.9	18.7	0.50	4σ-outlier test
σ [%]	127	39	23	92	42	66	
n	564	588	580	535	612	606	
Loss [%]	6	2	3	13	1	2	
Upper limit 2σ	41	5.7	0.07	35	39	1.5	
	Ni	Pb	Sc	Ni	Pb	Sc	
Mean	5.4	3.0		9.2	18.8	0.50	
Median	5.4	3.0		9.2	18.8	0.50	Calculated distribution
σ [%]	56	29	–	47	29	39	
n	598	598		618	618	618	
Upper limit 2σ	11.5	4.7	–	18	30	0.9	

the Norwegian data, while the Sc-values correspond fairly well with the Norwegian data. These results reflect the different lithologies in both regions and can be seen as plausible and realistic.

For the C-horizon in Norway, Reimann and Caritat (1998) give median values of 19.1 mg Ni kg^{-1}; 13 mg Pb kg^{-1} and 4.7 mg Sc kg^{-1}. Again, the Pb values from Kola are considerably lower, and the Ni and Sc values almost the same. This corresponds to the experience gained with the B-horizon and is again plausible and realistic. All test methods reduce the upper limit of the background in comparison to the original data set. This is particularly apparent with the 2σ-technique and with the calculated data set.

Conclusion

The quantification of a geochemical background, mainly for trace components, is necessary for both applied and theoretical (bio)geochemical questions and models. It makes little sense to use global background data – as important as they are for global models – to answer regional, or even more difficult, local problems. Therefore, the natural background will have to be evaluated for the individual task, provided that representative sampling is guaranteed. A new definition for the geochemical (natural) background formulates the resulting requirements leading to an appropriate approximation.

Considering the necessity to find a simple and robust statistical test, both the 2σ-technique and a calculated distribution present rather realistic data for the geochemical background in different data sets. All techniques lead to an approximation of mean and median values. The median value may differ strongly, depending upon the chosen technique. This is particularly true for the 2σ-approach. All techniques omit single values from the original data set with the smallest "losses" occurring with the 4σ-outlier test. The addition of the double, iteratively-calculated standard deviation of the fitted data set to its new mean value leads to a postulated upper limit of the background range. In most cases, the obtained values are

Table 4
Statistical parameters of the original data set of soil samples (mg kg^{-1}) from the Kola peninsula and their alteration through the application of three statistical methods to derive a natural background (see text)

	B-horizon			C-horizon			
	Ni	Pb	Sc	Ni	Pb	Sc	
Mean	19.5	3.9	2.74	23.4	2.7	2.82	
Median	16.1	3.0	2.60	18.6	1.6	2.30	Original data set
σ [%]	81	73	46	90	121	64	
Number n	578	578	578	605	604	605	
Upper limit 2σ	50	9.6	5.3	66	9.2	6.4	
	Ni	Pb	Sc	Ni	Pb	Sc	
Mean	12.9	2.6	2.46	16.2	1.4	2.06	
Median	12.5	2.5	2.50	15.4	1.4	2.10	2σ-method
σ [%]	40	28	34	43	30	36	
n	424	406	520	478	428	472	
Loss [%]	27	30	10	21	29	22	
Upper limit 2σ	23	4	4.1	30	2.2	3.5	
	Ni	Pb	Sc	Ni	Pb	Sc	
Mean	18.3	3.6	2.69	21.2	2.3	2.66	
Median	16.0	3.0	2.60	17.9	1.6	2.30	4σ-outlier test
σ [%]	61	58	41	59	76	54	
n	571	566	574	592	581	593	
Loss [%]	1	2	1	2	4	2	
Upper limit 2σ	41	7.8	4.9	46	5.8	5.5	
	Ni	Pb	Sc	Ni	Pb	Sc	
Mean	16.1	3.0	2.6	18.6	1.6	2.3	
Median	16.1	3.0	2.6	18.6	1.6	2.3	Calculated distribution
σ [%]	43	32	36	42	31	60	
Upper limit 2σ	30	4.9	4.5	34.2	2.6	5.1	

realistic and plausible (Fig. 8). This should not, however, lead to the conclusion that true or absolutely correct values can be quantified for the natural variability range. Errors may still be large (factor 2–3), but a higher precision may be neither feasable nor useful. Another restriction is the exclusion of alkaline, alkaline earth elements and halogens from this approach, since their environmental behaviour is not coherent with the initial assumptions. These limitations are relevant and have to be considered when applying the suggested methods. As long as the investigation for a natural background is done solely via the quantification of an analyte from the data set, the approach remains self-referential. An approximation in respect to high probability is possible, a robust proof remains impossible because most of the relevant variables of the natural system remain beyond discussion. Since the workload and costs involved for such investigations (e.g., quantification of paleo-element fluxes, isotope "fingerprinting", etc.) is mostly way too high, the tested methods are recommended as a fast and easy approach for any data set where natural influences shall be distinguished from anthropogenic ones.

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