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Geochemical background—concept and reality

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Abstract

The definitions and use of the term 'background' in exploration and environmental geochemistry are reviewed. Based on data from two subcontinental-scale geochemical mapping projects, it is shown that trying to define 'a background' for a large area is fraught with problems. It is demonstrated that background may change from area to area within a region and between regions. Although global averages are of general use, no specific global background levels of elements, for example in soils, can be defined, at best regional or local operational estimates can be made, though with caveats. Using background estimates based on concentrations in deeper soil levels to judge element concentrations in upper soil horizons (e.g., the TOP/BOT-ratio) can lead to severe misinterpretations if natural biogeochemical soil formation processes are ignored. Because of large natural variations in element concentrations in, for example soils, even the establishment of maximum admissible concentration based on ecotoxicological investigations is a difficult exercise. Organisms may become adapted to natural differences. Furthermore, there are challenges in converting the concentrations of the soluble substances used in ecotoxicological studies to appropriate levels in solid phase material, for example soils, analysed by commonly employed acid digestion procedures. Toxicological thresholds may thus also need to consider a spatial component that is presently neglected.

Keywords: Background; Baseline values; Threshold; Anomaly; Normal distribution; Regional geochemistry; Ecotoxicology

1. Introduction

The term 'geochemical background' comes originally from exploration geochemistry. Hawkes and Webb (1962) defined background as

(1) "the normal abundance of an element in barren earth material" and concluded "it is more realistic to view background as a range rather than an absolute value". The concept of geochemical background was introduced to differentiate between normal element concentrations and anomalies, which might be indicative of an ore occurrence:

(2) "By definition, an anomaly, is a deviation from the norm. A geochemical anomaly, more specifically, is a departure from the geochemical patterns that are normal for a given area or geochemical landscape" (Hawkes and Webb,

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1962). To be able to differentiate between background and anomaly, the term threshold was introduced,

(3) "the threshold is the upper limit of normal background fluctuation". One problem with this definition of background is the word normal, what is "normal abundance"? Another is the focus on 'high values' as identifying anomalies. A more general definition that acknowledges that low as well as high values, ratios and other computed criteria are commonly used to isolate anomalies from the main mass of data is that
(4) "Threshold is the outer limit of background variation" (Garrett, 1991).
In environmental geochemistry, there are also problems with the definition of 'background'. In a recent dictionary of environmental science and technology, Porteous (1996) provided the following definition:
(5) "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".
Another definition for 'background' in environmental sciences is,
(6) "the concentration of a substance in a sample material at a distance to a source where the concentration of the substance can no longer be proven to originate from this source".

It appears to be difficult to define 'background'; furthermore, definition (6) assumes a homogeneous regional (geo)chemistry where the only source of variation is due to the anthropogenic source being investigated. The latter appears to have been a widespread misconception among regulators, together with the perception that chemical elements are present naturally in the environment only at concentrations lower than man-made contamination. Whilst geochemists have been aware of the natural variability of elements in the environment for over 50 years, the more so due to national geochemical mapping exercises undertaken in the last 25 years. Thus, geochemists have the important task to provide data and maps on, and explain the concept of, background variations of elements to regulators and the general public. For example, the establishment of reliable background concentrations of chemical elements in soil has been an important issue in environmental sciences. In the United States of America, background concentrations are often used as soil clean-up criteria following industrial activities. 'Background' would here be defined as:

(7) "the elemental concentration(s) before industrialisation", which was usually not documented. This implies the availability of reliable procedures to distinguish between "natural" and "man-made" element concentrations in soils (and other environmental materials). Finding equivalent "archival" material that has not undergone chemical changes, diagenesis, post-formation or deposition is difficult. Environmental materials are part of a "living" system in an overall biogeochemical cycle, instances where materials have been frozen-in-time are rare. Alternately, isotopic and multi-element (multivariate) statistical procedures can sometimes discriminate between elemental patterns of natural and anthropogenic origin that can be used to estimate pre-anthropogenic element levels.

The term

(8) 'natural background' is widely used to infer 'background' levels reflecting natural processes uninfluenced by human activities.

However, there is evidence from the world's ice sheets and glaciers that small amounts of elements have been transported on intercontinental scales to remote regions and deposited as a result of being released into the atmosphere due to human activity. Similarly, large masses of natural materials are released into the atmosphere and transported intercontinentally from volcanic eruptions and dust from desert windstorms. Both effects will alter the natural background at the location where the material is deposited, independent of natural or anthropogenic source. Should both be viewed as 'contamination'? Can nature 'contaminate' nature? Surely this is part of the natural evolution of the Earth, the biogeochemical cycle. In a practical sense, beyond some distance from an anthropogenic source the amounts deposited to mineral and biological surfaces are so small that they do not mask the variation present due to natural biogeochemical processes (definition (6) above). The Kola Ecogeochemistry Project (Reimann et al., 1998) has provided evidence that even around major industrial sites their recognizable footprint for most measurable substances in soil, moss, water and even snow and rain extends only a few hundred, and not thousands of, kilometres. Is 'background' a question of scale?

Sometimes the term

(9) 'ambient background' is used to describe the unmeasurably perturbed and no longer pristine 'natural background'.

However, this term is also appropriate for a local modified 'background' in an area close to human activity. It can be argued that many slightly elevated levels in soils and sediments in areas of the world that have a long history of human occupation, agriculture, and latterly industry, e.g., areas in Europe, reflect 'ambient background' and are no longer 'natural'. There is a fine line to be drawn here, and maybe the practical approach is to continue to use the term 'natural background' if natural processes can still be discerned in the data, and 'ambient background' when natural processes become obscured. However, it can be argued that 'natural background' no longer exists on this planet.

The term

(10) 'pre-industrial background' is sometimes used when data either come from age-dated materials or are collected from areas believed to represent a survey/study area in its supposed 'pre-industrialization' state.

Care needs to be taken in making such extrapolations to ensure, in the first instance, that post-depositional processes have not modified the biogeochemical patterns, and in the latter case, that the area believed to represent the area of interest is sufficiently biogeochemically similar to be considered a valid surrogate.

Lastly, the term

(11) 'baseline' is sometimes used in equivalency to 'background', or correctly 'ambient background' as is used in the context of measuring levels 'now' so that future change can be quantified.

This is an important issue (e.g., Darnley et al., 1995; Garrett, 2003); however, in the authors' opinion, the use of the term 'baseline' gives the impression that there is a single number, 'line', where in fact there are a range of values characterizing any particular area or region reflecting the heterogeneity of the environment. This was recognized by Darnley et al. (1995) who following mention of the fact that "an increasing number of jurisdictions have been engaged in the development of quantitative criteria relating to trace constituents in soil water and sediment" state that, "In a number of instances little attention has been paid to variability. . .". Ending with the observation that this was due to the fact that "use of terms such as 'baseline value' has often been assumed to imply that the natural background level for each element is constant". Therefore, we do not support the use of the term 'baseline'.

A completely different approach is to set regulatory levels (action levels, maximum admissible concentration values (MAC-values)) for environmental purposes externally on the basis of ecotoxicological studies and risk assessments (e.g., Janssen et al., 2000; Allen, 2002). The challenge with this approach is translating the results of ecotoxicological studies that use soluble salts into appropriate levels in the solid-phase materials, soils and sediments, in terms of the measurement protocols used, i.e., size fraction and method of analysis. When this 'translation' is inappropriate ecotoxicologically based levels can be set down into the range of natural background levels. When this happens and there is no evidence of biological harm or disturbance to the ecosystem, the whole procedure comes under suspicion. Regulatory levels, once set by a state authority, have important financial consequences. For example, clean-up to levels below the natural occurring concentrations can be prohibitively expensive, usually makes no sense, and will likely damage the ecosystem to be protected.

There exist cases where natural elevated element concentrations can genuinely pose a risk to human health. One example is natural high concentrations of As in drinking water wells in India and Bangladesh (i.e., arsenosis, Das et al., 1995; Smith et al., 2000). On a world-wide scale, and just as important, but widely neglected there exist cases where too low natural concentrations of elements in drinking water, soils or crops pose a severe health risk to the general population (e.g., selenosis, Tan, 1989; Combs et al., 1996). In an ideal world, the regulatory levels would preserve the ecosystems they are set to protect. This would include avoiding unnecessary remediation that could be destructive to the very environment to be protected, e.g., special plant communities developed on ultramafic rocks where soils display high Mg levels and Cr and Ni concentrations far beyond ecotoxicologically set levels for other less rare and exotic soils (Brooks et al., 1995). In that context, regulatory levels could even be set, in a framework of ecotoxicological considerations, above the upper limits of natural background variation if natural background levels did not cause ecosystem damage. It can be argued that natural background levels never cause ecosystem damage, as, in the case of ultramafic rocks, a unique ecosystem has developed that relies on the unusual environment for its existence. Incompatibility problems arise when biota exotic to an environment being studied are used in ecotoxicological experiments, or have been insufficiently acclimated as would occur naturally. Any definition of a regulatory level should be accompanied by an explanation of how it was derived and the issues taken into consideration. In some instances, the 'loose use' of terminology results in the upper limit being referred to as 'background'; this is incorrect and should be avoided as it just contributes to miscommunication. To cover all deleterious situations, it would be necessary to define another set of regulatory 'lower' levels to avoid deficiency-related problems. Can the solution then be a blend of risk assessment and statistical or visual definition of 'natural background'?

In this section, we have reviewed the history of 'background', 'anomaly' and 'threshold', and discussed the concepts of 'background' and "normal abundance". In the next sections, we will present the regional distribution of some elements in soils at a range of map scales and approach the concept of 'background' from the subcontinental to the local site-related scale. The examples will demonstrate that the idea of being able to define 'background' via a statistical exercise (for a discussion of methods used, see Reimann et al., in press) alone is illusive. To estimate the properties of 'background', the presence of, or complete absence of, anomalous samples (outliers), spatial scale, location, the kind of sample material, and why and for what purpose the 'background' is needed all have to be considered. This implies that no single background range exists for any one element in any sample material except for specific, often spatially local, instances. 'Background' may change both within a project area and between project areas—reflecting the diversity of the physical world. We will show examples of natural variation of elements on different scales and discuss difficulties in defining a 'background' or 'threshold', and even of setting regulatory levels based on toxicological consideration alone. The conclusion is that geochemical maps at different scales covering a variety of sample materials and the whole surface area of the planet are needed as basic information for society—just like geological, geophysical and topographical maps.

2. Materials and methods

Data from two different scale geochemical surveys carried out in Europe during the last decade will be used to demonstrate the variability of 'background'.

The first data set comes from the subcontinental-scale Baltic Soil Survey (BSS-Project, Reimann et al., 2003). Two horizons of agricultural soils, the A_p-horizon (0–25 cm, TOP) and the B/C-horizon (50–75 cm, BOTtom) were collected at ca. 750 sites within a 1.8 million km^2 area, covering a large part of northern Europe (Fig. 1). All details on the project, quality control, the original data set and regional distribution maps for 62 elements in the <2 mm fraction can be found in Reimann et al. (2003).

The second data set comes from the Kola Ecogeochemistry Project (Reimann et al., 1998). Terrestrial moss and different horizons (O-, B- and C-) of podsol profiles were collected at ca.

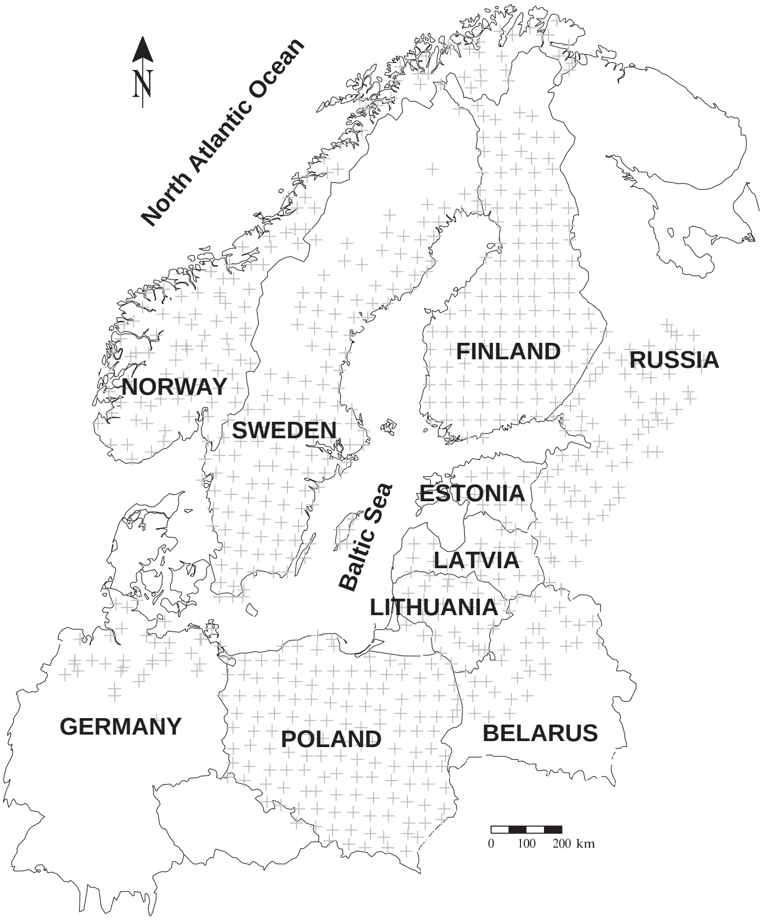

Fig. 1. Area of the Baltic Soil Survey (BSS-Project). Grey crosses mark the sample locations within the 10 countries.

600 sites within a 188,000 km^2 area in the European Arctic (Fig. 2) covering environments ranging from heavily polluted (surroundings of Monchegorsk, Nikel and Zapoljarnij in Russia) to almost pristine (northern Finland and Norway). All details on sampling, analyses, quality control and regional distribution maps for all elements in all sample materials are given in Reimann et al. (1998).

2.1. Methods used to determine 'background', 'threshold' and 'anomaly'

Hawkes and Webb (1962) proposed three procedures that could be used to identify and select a threshold value: (i) In areas of known mineral occurrences, carry out an orientation survey around and away from the mineral occurrence(s) and plot the data as maps, histograms and/or cumulative frequency plots, and select by eye the best value that differentiates mineral occurrence-related data from the remainder. (ii) Where no such a priori information was available or if there were no obvious anomalies and the data followed a generally gaussian distribution, if necessary after a logarithmic transform, that "the threshold for that material may be conventionally taken as the mean plus twice the standard deviation. That is equivalent to saying that only 1 in 40 background samples is likely to exceed the threshold content". (iii) Where the data sets were small or "where the statistical distribution is irregular, probably the best approximation is to take the median value as

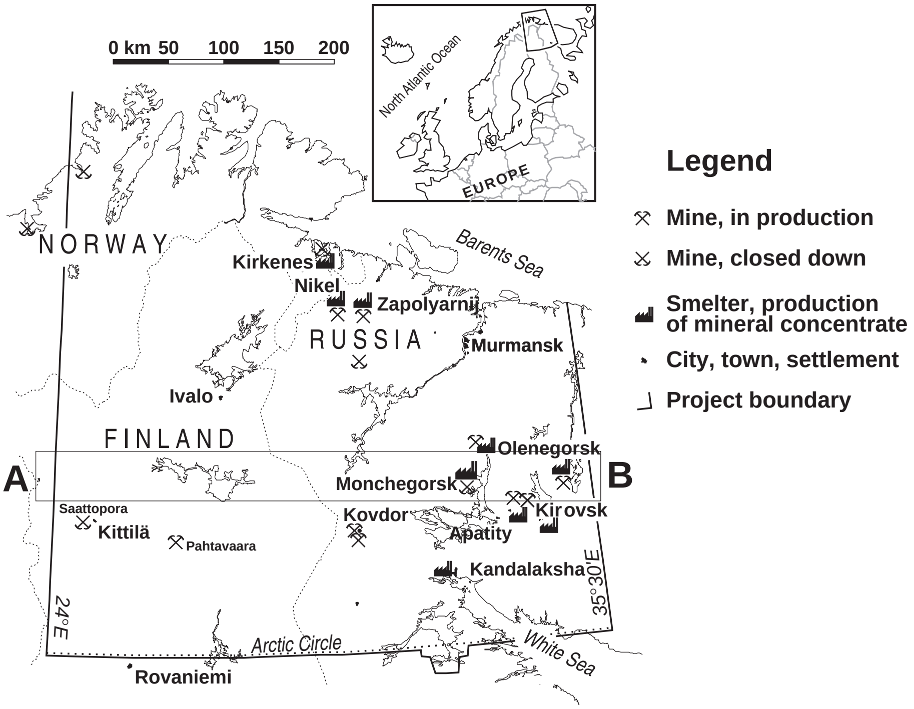

Fig. 2. Area of the Kola Ecogeochemistry Project. A–B marks the location of the E–W-transect through Monchegorsk used to construct the profiles in Fig. 7.

'background' and to estimate threshold as that value which is exceeded by no more than 2½% of the total number of observations, excluding markedly high erratic values". In the accompanying table (2–8, p. 31) this is referred to as "a method for estimating a provisional value for threshold from limited background data". With reference to the above, it must be remembered that these methods were proposed in the pre-digital-computer era, when pencil-and-paper, log tables and slide-rules were all that were available to most scientists; and means and standard deviations for large data sets were estimated by the 'grouped frequencies' procedure (e.g., Moroney, 1965), made easy once a histogram had been prepared. Method (ii) should never be used today as computers are freely available to undertake method (iii). Recently, Reimann et al. (in press) reviewed the validity and performance of statistical methods to determine 'background' and 'threshold', and concluded that orientation surveys are needed in addition to the graphical display of results in maps and cumulative distribution plots. Of the statically oriented methods, the boxplot as defined by Tukey (1977) will perform best as long as outliers comprise less than 15% of a data set (Reimann et al., in press).

3. Results and discussion

Starting at the subcontinental scale, Fig. 3 shows the regional distribution of the element V in the A_p-horizon (TOP) and the B/C-horizon (BOT) of agricultural soils from the BSS-Project (Reimann et al., 2003). High V concentrations dominate northwestern Scandinavia (all of Norway and northern Sweden), whereas low concentrations occur throughout the southern part of the project area (N-Germany, Poland, Belarus, the three Baltic States and the southern part of the Russian project area). Fig. 4 presents the same data as a Tukey boxplot comparison of element concentrations and variation in the 10 countries sampled. Whereas the median V concentration in Norway is 79 mg/kg, the median concentration in Belarus is 17 mg/kg, a factor of

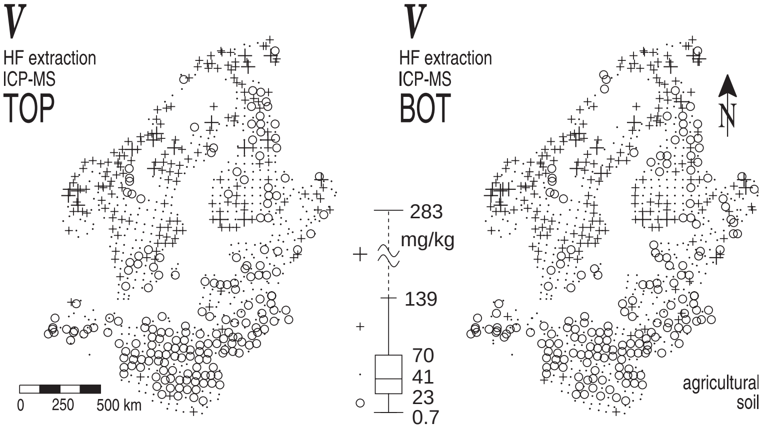

Fig. 3. Regional distribution of V in the BSS-Project area. TOP: A_p-horizon, 0–25 cm; BOT: B/C-horizon, 50–75 cm. The boxplot used for class selection is the original Tukey boxplot (Tukey, 1977); the box indicates approximately the 25th, 50th and 75th percentile; outliers are defined according to: (upper whisker, lower whisker) = (upper hinge, lower hinge) ± 1.5 × hingespread and do thus not indicate a defined percentile but depend on the distribution of the inner 50% of the data.

almost 5 (4.6). There are also large differences in variation between the countries, the Nordic countries (Norway, Finland, Sweden, partly Russia) displaying a much higher variation than all others. What, then, is the background variation, i.e., the range of the background values, and, in particular, the upper limit that might be a candidate for a regulatory level for V in agricultural soils in northern Europe? It is clear that statistically derived values from the whole data will not be locally appropriate. All the outliers (anomalies) would occur in Norway and none would ever be found in Poland (except for some instance of gross contamination). Fig. 3 demonstrates that regional variation in the data displayed in the subcontinental-scale map must be due to natural differences; it cannot be linked to industry, power plants or other human activities. In Norway, many of the high values can be attributed to the occurrence of greenstones, rocks naturally rich in Fe–Mg alumino-silicate minerals that contain transition metals. The high levels in the northern part of the Russian project area are linked to the occurrence of black shales and, in South Finland and Sweden, high V levels are most likely related to clay-rich soils (Reimann et al., 2003). Thus, even with a 100% natural distribution, it is impossible to establish a single background range for the survey area. The natural differences in V distribution across the survey area are too large; in the geochemical

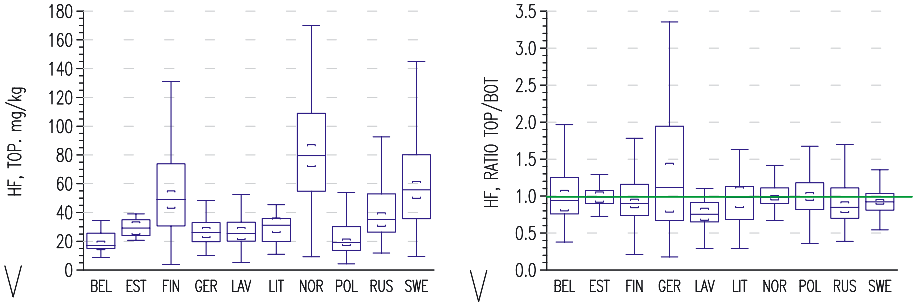

Fig. 4. Boxplot comparison of V in agricultural soils from 10 countries surrounding the Baltic Sea (BEL: western Belarus, EST: Estonia, FIN: Finland, GER: northern Germany, LAV: Latvia, LIT: Lithuania, NOR: Norway, POL: Poland, RUS: western Russia, SWE: Sweden). Left: V concentrations in the TOP-layer (A_p-horizon, 0–25cm); right: ratio between TOP and BOTtom (B/C-horizon, 50–75 cm) layer.

context, the survey area is too heterogeneous for a single background range to be scientifically supportable. Fig. 4 also shows the TOP/BOT-ratio and that the medians are close to unity for the different countries. However, the variation in the ratio is unusually large in Germany, indicating the presence of a process that leads to elevated levels in the surface soil, possibly contamination. However, these sites in Germany do not stand out as high values in the map because much higher natural values exist over large parts of Norway and Sweden. These natural concentrations in Scandinavia exceed by far what may be caused by contamination in Germany-detailed investigations on a local scale would be needed, and a background-value taken from a 'North-Europe map' clearly has no relevance.

The alternative approach would be to work with a toxicology-derived threshold value to determine whether any of the V values are above a safe-for-ecosystem-health-level. It is, however, a fundamental question as to whether a single toxicological evaluation would be relevant if it did not take into account that there is a factor of 5 difference in the median values between the countries. This is important, as there may be different acclimated biological communities forming healthy ecosystems present in different 'background' areas; and, to be realistic and relevant, ecotoxicological studies should be undertaken with those species in appropriate ambient media. Thus, it may be that organisms in Norway are adapted to these relatively high V levels, which might be toxic to the same organisms from Poland. Furthermore, the Norwegian organisms might suffer from V-deficiency if subjected to the low V levels present in Poland.

The map of V distribution (Fig. 3) suggests that it would be sensible to define class boundaries that lead to more homogenous data subsets, e.g., (1) Norway and Sweden, (2) Finland and Russia, and (3) the Baltic States, Belarus, Poland and North-Germany. These national divisions may seem to have little relevance to geochemistry. However, they reflect several physical factors: the dominance of (1) Caledonian and Precambrian, (2) Precambrian and (3) younger Phanerozoic rocks, respectively; a change in biophysical characteristics from tundra and coniferous forests and a sub-arctic climate in the north, (1) and (2), to deciduous forests and a more temperate climate in the south, (3). Thus, these national divisions reflect different biogeochemical domains. When this subdivision is applied, the resulting map (Fig. 5) reveals far more detail. However, this requires that in one and the same map boxplots (the upper whisker of the boxplot taken as the statistically defined threshold, dividing background variation from anomalies, Reimann et al., in press) be used to define three widely different upper limits of 'background', in the case of V: 170, 125 and 55 mg/kg. The advantage is that local deviations in the different subsets are far more visible in the resulting map (Fig. 5). For example, it is possible to see a clear increase of V values towards the southern border of Poland. This is most likely due to parallel changes in geology and from sandy to more clayey soils in the south. The three outliers (large crosses) may actually be due to contamination and would have to be checked against a map of industrial activity. In Germany, there is clear structure in the data, with several outliers in the northernmost part. These would again need to be checked against the location of possible anthropogenic sources (e.g., oil or coal burning power stations, refineries).

The example demonstrates that for the definition of a meaningful background range, and in particular its upper limit, a statistical procedure alone cannot work. More than just geochemical information is needed to understand the sources and processes behind the broad spatial variation patterns and the causes of individual high values. The inference has to be that contamination and pollution processes are on a local scale relative to natural fluctuations in element levels due to biogeochemical processes. The large continental-scale regional variability makes it impossible to define any useful measure of background variation, and its upper limit (threshold), for an area such as northern Europe (1.8 million km^2). Maps at this scale are, however, needed to provide context to any local investigation.

The Kola Project (Reimann et al., 1998) mapped a smaller area (188,000 km^2) that included several major point source emitters, e.g., the nickel smelters in Monchegorsk and Nikel-Zapoljarnij (for locations, see Fig. 2), at a higher density (1 site per 300 km^2). Bismuth, a rare trace element, is emitted in minor amounts by the Monchegorsk refinery and even less by the Nikel-Zapoljarnij smelter and roaster. Because

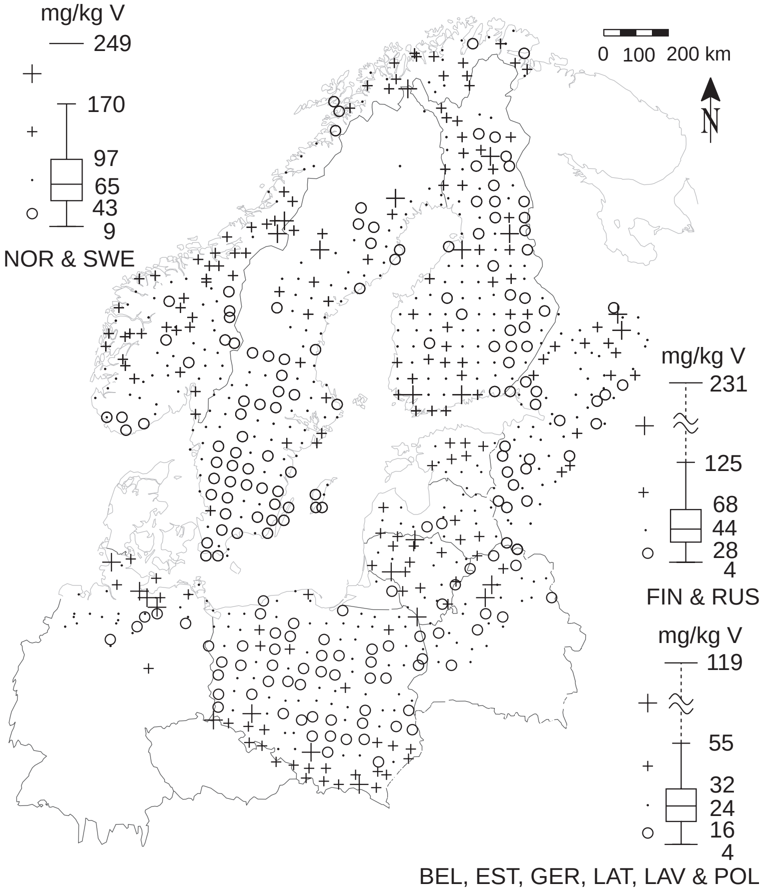

Fig. 5. Regional V distribution in the TOP-layer of agricultural soils, class selection via boxplots (see Fig. 3) according to the large groups displaying different concentration levels in the map given in Fig. 3: Norway and Sweden, Russia and Finland, and all other countries.

of its rarity Bi is well suited to study the impact emissions have on the local environment and on 'background', using a variety of different sample materials.

Fig. 6 shows maps of the Bi-distribution in moss, and the O- and C-horizons for the Kola area (from Reimann et al., 1998). When using moss for mapping the impact of the Monchegorsk refinery, its presence dominates the spatial distribution of Bi levels (Fig. 6A); it is straightforward to deduce from the map that the background range for Bi in moss is between <0.004 mg/kg and 0.029 mg/kg (which is the 75th percentile). As expected (from the known composition of the ore feed), the anomaly related to Nikel and Zapoljarnij is much smaller than at Monchegorsk, but there are still many values above 0.029 mg/kg.

The story becomes more complicated when using the O-horizon for mapping. The map (Fig. 6B) shows a smaller anomaly around Monchegorsk and a small group of outliers near Nikel. However, and more importantly, the map is dominated by a prominent north–south gradient, with ever increasing Bi levels towards the south. This distribution is due to climate and bioproductivity, and as such is a natural phenomenon (Reimann et al., 2000, 2001a). It is no longer possible to define a clear border between 'background' and 'anomaly', natural values and the effects of contamination. 'Background' near the northern coast is low (<0.12 mg/kg) and in the southern third of the survey area is much higher (>0.22 mg/kg).

The map for the C-horizon soils (Fig. 6C) shows a completely different distribution. The highest levels

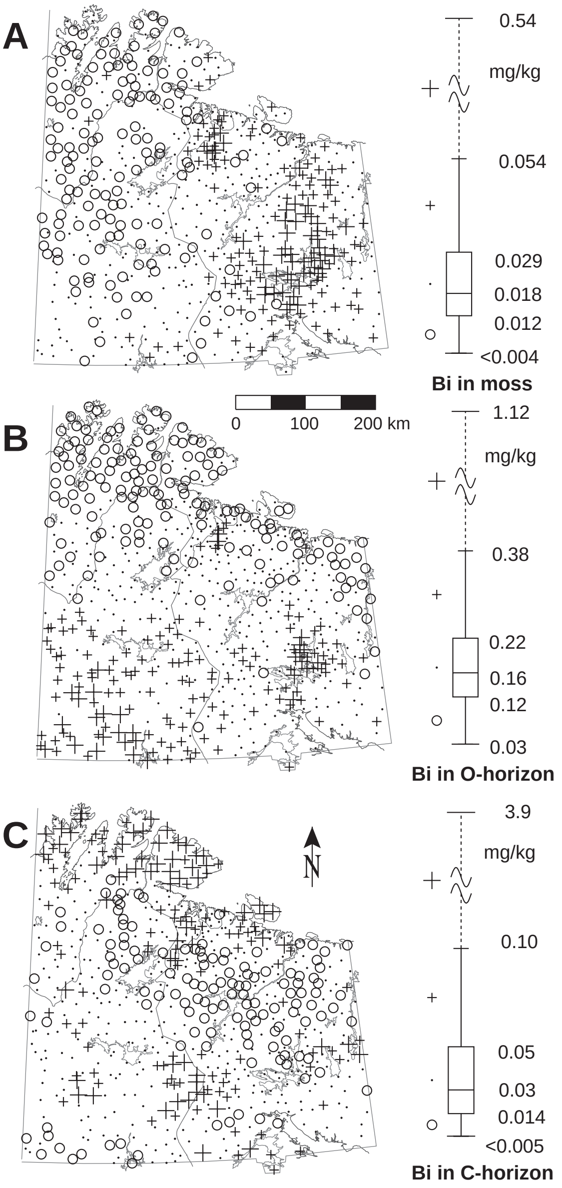

Fig. 6. Bismuth-distribution in terrestrial moss (*Hylocomium splendens* and *Pleurozium schreberi*) and O- and C-horizon soil samples in the Kola Project area. For location of industrial sites and other locations named in the text, see Fig. 2.

occur on Caledonian sediments along the Norwegian coast and overlying a pegmatite field along the Finnish–Russian border. Other locally high levels correlate with the presence of unusual rocks (alkaline intrusions near Apatity) or mineralisation-related events (central Finnish project area) (Reimann and Melezhik, 2001). The map demonstrates that no single regional background range exists, but that there are several sizeable areas with different ranges of Bi concentrations. Division of the project area into ‘biogeochemical domains’ would result in the C-horizon ‘anomaly’ in the Norwegian part of the survey area no longer being an ‘anomaly’, such Bi levels would be normal for the area. One clear conclusion that can be drawn from these three maps is that contamination has not yet reached the deeper soil layers. A further clear message from these maps is that the deeper soil layers cannot reliably be used to deduce the natural, uncontaminated, Bi concentrations in surface soils.

An alternate approach to visualise ‘background’ and ‘contamination/anomaly’ around a clearly defined anthropogenic source such as Monchegorsk is to draw profiles across the expected source and study the distribution of the elements with distance from the source (e.g., Reimann et al., 1997, McMartin et al., 2002). Fig. 7 shows a number of such profiles for the O-horizon transecting Monchegorsk in an east–west direction. For most of the elements, the influence of Monchegorsk is easily visible–as well as the distance to the point where this influence disappears into the background variation–often at less than 50 km (e.g., Ag, As, Bi) and up to 150 km (Cu, Ni) from source. For Pb, the profile shows that the Pb emissions from Monchegorsk would not be discerned within the background variation were it not plotted as a profile. Apatity, some 30 km east of Monchegorsk, appears as a second source of Pb. Near the western project boundary (-300 km on the x-axis), the profile intersects a geogenic Pb anomaly related to hydrothermal alteration (Reimann and Melezhik, 2001), reaching levels almost as high as observed near Monchegorsk. The profile for Zn shows that no recognizable Zn is emitted at Monchegorsk, the highest levels occur near Apatity. Such simple profiles, which come close to a graphical display of definition (6) of ‘background’, are a much better indication of the influence of contamination than any statistically derived background variation estimates.

Table 1 summarises a number of arsenic median values from soil surveys in different parts of the world. The size of the area mapped varies from some

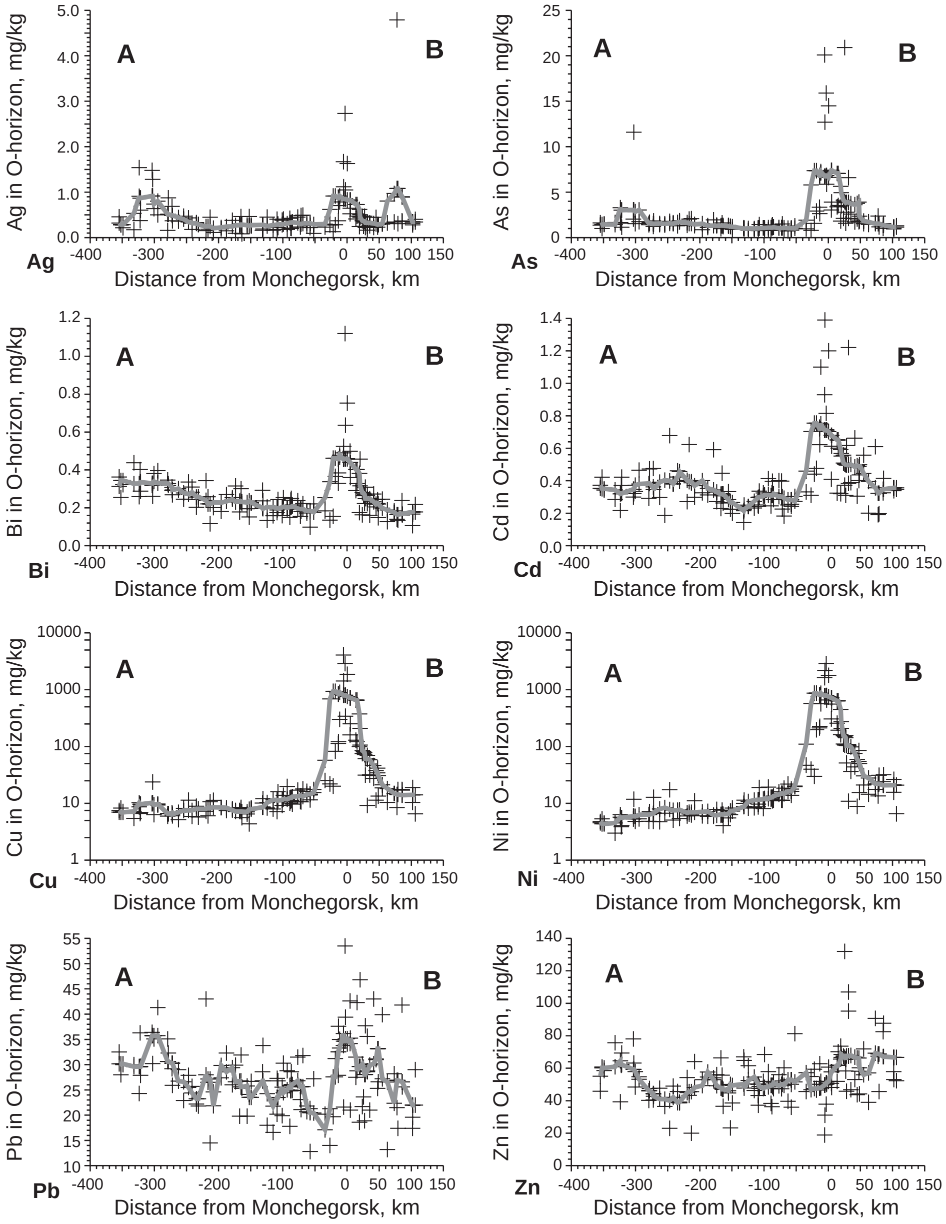

Fig. 7. East–west profiles through the Kola Project area, cutting the nickel refinery at Monchegorsk (see Fig. 2 for location). For meteorological details (wind directions during the year, precipitation), see Reimann et al. (1998).

tens to hundreds of thousands and millions of square kilometres. Although differences in grain size and analytical method may account for some of the variation in the results by far the largest factor is geographic location. Levels observed in Austria, for example, are 6 to 20 times above the world average. Table 2 shows some soil clean-up levels as defined by different authorities around the world. Considering the values in Tables 1 and 2, one could ask, “Are large areas of Austria seriously contaminated, do these have to be remediated?” The answer is, of course, “No”; Austria just happens to lie in an As-geochemical

Table 1
As (mg/kg) concentrations in soils from different parts of the world

Area	Fraction and analysis	As (mg/kg)	Data source
World	<2 mm, total	5	1
USA, surface soil	<2 mm, total	5.6	2
Canada, Prairies, Ap-horizon	<2 mm, total	6.6	3
Finland, Till (C-horizon)	<0.063 mm, total	2.6	1
Australia, Laterite	0.45–2 mm, total	3	4
Jamaica, surface soil	<0.15 mm, total	16	5
Austria, Walchen, B-horizon	<0.18 mm, total	30	6
Austria, Saualpe, B-horizon	<2 mm, aqua regia	101	7
Austria, Saualpe, B-horizon	<0.18 mm, aqua regia	115	7
Austria, Wechsel, B-horizon	<2 mm, total	29	8
Kola, C-horizon	<2 mm, aqua regia	0.5	9
Kola, B-horizon	<2 mm, aqua regia	1.1	9
Kola, O-horizon	<2 mm, conc. HNO$_3$	1.2	9
Northern Europe, Ap-horizon	<2 mm, aqua regia	1.9	10
Northern Europe, B/C-horizon	<2 mm, aqua regia	2	10
Slovak Republic, A-horizon	<2 mm, total	7.2	11
Slovak Republic, C-horizon	<2 mm, total	6.6	11
Germany, Saxony, topsoil	<2 mm, total	12	12
Germany, Saxony, subsoil	<2 mm, total	9	12
Lithuania, topsoil	<2 mm, total	2.4	13
Florida, surface soil	<2 mm, HCl–HNO$_3$–HF	0.42	14

Data sources: (1) Koljonen (1992), (2) Gustavsson et al. (2001), (3) Reimann and de Caritat (1998), (4) Smith et al. (1992), (5) Lalor et al. (1995), (6) Reimann (1989), (7) Göd (1994), (8) Göd and Heiss (1996), (9) Reimann et al. (1998), (10) Reimann et al. (2003), (11) Čurlik and Šefčik (1999), (12) Rank et al. (1999), (13) Kadunas et al. (1999), (14) Chen et al. (2001).

province and has sizeable areas with high natural As concentrations. A risk level could only be established after careful study of the mineralogy of the samples to understand how the As is bound and whether or not, and under what circumstances, it may be bioaccessible and able to damage the ecosystem. Clean-up activities without such investigation, just carried out because a statistically derived trigger value is met, may well worsen the environmental situation. High and low values alone and statistically derived risk levels are not well suited to differentiate between 'clean' or 'natural' and 'contaminated' environments without auxiliary displays, e.g., maps and profiles, and information.

3.1. Are TOP/BOT-ratios a reliable tool to distinguish between 'background' and 'contamination'?

Some authors (e.g., Steinnes and Njåstad, 1995; Blaser et al., 2000) suggest that element concentrations measured in a deeper soil horizon can be taken as 'local background' for the upper soil horizons that are more likely affected by anthropogenic contamination. Considerably higher metal values in overlying soil horizons are often interpreted as evidence of anthropogenic contamination.

A TOP/BOT-ratio as an indication of relative enrichment/depletion of elements in the uppermost soil layer may, to a certain extent, make sense on agricultural land. Here both layers, the A$_p$-horizon (TOP) and the deeper soil horizons B- and/or C-horizons (BOT), are predominantly mineral soil.

Table 2
Arsenic (mg/kg) clean-up levels as defined by different public authorities

Distributionally defined levels	
Canada, Ontario ministry of the environment	
Agricultural land	25
Industrial land	50
Residential soil	25
U.K.	
Domestic gardens	10
Parks, open land	40
U.S.A.	
USEPA soil screening level	0.40
Florida soil clean-up goal	
Residential	0.8
Industrial	3.7
Toxicologically defined risk levels	
Germany	
(a) As in kindergarden soil	25
(b) As in kindergarden soil, check	20
(c) As in kindergarden soil, immediate action	50
Norway	
As in kindergarden soil/sand	20

Data sources: Canada: Arnt et al. (1997); U.K.: O'Neill (1990); U.S.A.: USEPA (1996) and FDEP Tonner-Navarro et al. (1998); Germany: (a) BbodSch (1999) (at time of writing the only valid value for Germany), (b and c) Metalle auf Kinderspielplätzen (1990); Norway: Langedal and Hellesnes (1997) and Ottesen et al. (1999).

However, even for agricultural soil, a high value in the TOP/BOT-ratio is no proof of contamination or other human interferences because the TOP-layer is not 1:1 comparable to the BOT-layer. It contains considerably more organic material. Many elements bind strongly with organic material and are enriched in more organic soils, as first observed by Goldschmidt (1937). In addition, the TOP-layer is often relatively depleted in the fine fraction (clay-size particles and oxyhydroxides), a process known as lessivation. Clay size particles as well as iron and manganese oxyhydroxides commonly contain much higher metal concentrations than the coarser soil size fractions. This process can lead to their relative depletion in the TOP-layer.

Evidence from the BSS data (Reimann et al., 2003) demonstrates that only 9 (out of 60 analysed) elements show a general enrichment in the TOP-layer. These are S (4×), Cd (2.2×), P (1.9×), LOI (1.8×), Se (1.8×), Pb (1.6×), Zn (1.4×), Bi (1.3×), Sb (1.3×) and Mn (1.2×). This combination of elements indicates that contamination is not the most likely explanation for the enrichment. Phosphorus, S, and probably Zn, Mn and Se, are often correlated to the abundance of organic matter (LOI). For Cd, Pb, Bi and Sb, the explanation that the enrichment is due to atmospheric input may be suggested. However, where are all the other elements that should also be enriched as well if atmospheric input and anthropogenic contamination is the most likely explanation for the enrichment: e.g., As, Co, Cu, Cr, Ni and V? The likely explanation is that the TOP/BOT-ratio of agricultural soils is predominantly related to type and amount of the organic fraction in the TOP-soils.

The uppermost horizon of forest soils consists predominantly of decaying organic matter and is, as such, not directly comparable to mineral soil horizons (e.g., Goldschmidt, 1937). Element concentrations observed in the humus layer can depend on the substrate, the plant community at the sample site (each plant has different characteristics with regards to uptake or rejection of elements, e.g., Kovaleskii, 1979; Brooks et al., 1983; Reimann et al., 2001b), tendency to organic binding and/or methylation, and atmospheric input of elements; these factors make data interpretation difficult.

For the Kola Project (Reimann et al., 1998), forest soils were collected. The O/C-horizon ratio shows a relative enrichment of S, Ag, Cd, Pb, Bi, Sb, Si, Sr, As, P and Zn in the O-horizon of the project area. The four elements that are actually emitted in major amounts in this area, Co, Cu, Ni and V are all missing from this list of elements enriched in the O-horizon relative to the C-horizon. Reimann et al. (2001a) demonstrate that practically no correlation exists between the element concentrations in the O- and C-horizon. Thus, the C-horizon cannot serve as an estimate of local 'background' for the O-horizon. Using the TOP/BOT-ratio as an indication of contamination would lead to an entirely erroneous interpretation. Again, the type and amount of organic material, organic binding and methylation are the predominant processes causing the enrichment of many of above elements in the O-horizon.

4. Conclusions

It is important that regulators recognize that 'background' depends on location and scale. It changes from area to area and with the scale of the area investigated. When mapping at the continental scale, natural element concentrations can be as high or even higher than any visible anthropogenic contamination. Natural variation of element concentrations in different environmental sample materials will often be so large that it is difficult to identify anthropogenic additions, contamination, in other than gross cases. These will usually be restricted to the local scale.

Only when 'local' information is unavailable, and none can be acquired for whatever reasons, is it necessary to resort to data generated in surveys from different parts of the world covering spatially significant areas. Such values are compiled, for example, in Reimann and de Caritat (1998), that importantly includes indications of range whenever available. Such estimates can give a first indication of whether results from a new investigation are in a 'likely' range and reflect the natural variations in concentrations present in different environments. However, in the end, only a properly constructed map and data analysis (Reimann, in press) will provide the required information concerning sources and sinks of chemical elements in the environment.

General indications can be provided, e.g., by presenting median values for world soils. Such values, however, as given in Table 2 ignore that 'background' is a range, not a single value. A statistically derived background value and associated range cannot be used alone to detect anthropogenic influences on the environment, geochemical mapping at an appropriate scale is essential. A well-constructed map will identify areas of relatively homogeneous geochemistry and permit, with other relevant information, the natural or anthropogenic processes governing the distribution of any one element to be deduced. Ideally, geochemical mapping should start at the continental scale, and continue to the national and finally local scale in areas of concern. Mapping has to start at the continental scale because experience teaches that geochemical data are usually not comparable across national borders. It is also most cost-effective to start at the scale that requires the lowest sample density. Such continental-scale maps should be the underpinning of much environmental geochemical research. Without recognition of the continental-scale geochemical patterns interpretations at local scales may be seriously misguided. Provision of such continental-scale background data is a clear, and largely up to now neglected, task for Geological Survey organisations (Darnley et al., 1995; Garrett, 2003). Ultimately mapping at many different scales will be necessary to determine site-specific 'backgrounds' and to be able to fully understand the processes that cause deviations from 'background'.

To establish 'normal abundance' or 'background' concentrations for a sample material in a study area a substantial number of samples have to be collected over a sufficiently large area to be able to differentiate between different possible natural and anthropogenic sources. Thus we are back to suggestion i) of Hawkes and Webb (1962), the orientation survey. Or as we have shown here; a careful regional survey approach where on the basis of mapping the region is subdivided into relatively homogeneous sub-areas, 'biogeochemical domains', related to specific natural subdivisions, i.e., a holistic ecosystem approach. These two approaches, one site specific and one regional, permit operationally defined background ranges to be estimated. However, before these can be accepted as risk or regulatory levels they have to be considered in the light of bioaccessibility and ecotoxicological studies. For example, it may be that the upper limit of background variation is far below the level where any ecotoxicological impact would be expected. Alternatively, if natural levels of some metals are high enough to impact some biota, specific populations of metal-resistant species can establish themselves and become the local normal ecosystem (for example on ultramafic rocks, Brooks et al., 1995).

An important issue neglected by many regulators, not fully aware of the range of natural variability, is that not only high values and anthropogenic pollution may represent a threat to human health: on a worldwide scale, element deficiency-related health problems may well be the more important human-health problem. Studies at the lower end of background variation and setting lower, minimum admissible concentration values (MICs) might have a greater impact on the overall health of the population of this planet than the present focus on high values and toxicity.

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