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Chapter 6

Diffuse soil contamination by antimony

6.1 Introduction

For antimony, eight regional- to continental-scale geochemical datasets establish reliable concentration statistics in top- and subsoil from different parts of the world: Australia, the United States, Europe. Comparing the statistical distributions of antimony in these two soil layers by means of cumulative probability (CP) plots provides several quantitative constraints for the relative importance of natural versus anthropogenic influences – with a focus on Europe. It is relatively easy to detect major localized contamination sources like metal smelters by geochemical mapping in their surroundings at the local to regional scale (e.g., [1, 2]). To estimate the input of elements to soil from non-local or diffuse contamination, for example, via long-range atmospheric transport, is much more challenging. Because the Euro-pean Commission has identified diffuse pollution as one of the eight major threats to soil quality [3] it is important to estimate this input. Only in a second step can it then be decided if this diffuse contamination fits a generally accepted definition of diffuse pollution, a term that is often used imprecisely in environmental sciences. Pollution implies that the contaminant has a biological impact. The distinction between contamination and pollution is essential for elements where an anthropo-genic contamination overlays a high natural background variation and has no biological effect, such that there is no diffuse pollution of soil, even if contamination can be detected.

Many authors have tried to establish the impact of anthropogenic contamination of an element in soil by (1) comparing measured values to upper crust concentrations (e.g., from [4]), and by (2) using ratios of element concentrations in top- and subsoil (e.g., [5, 6]), or 3) by defining more elaborate ratios like geoaccumulation indices, contamination factors, or enrichment factors (EFs – e.g., [7]). However, none of these ratios or factors can work in other than extreme cases of soil contamination, because the assumptions underlying their calculation neglect basic principles of soil formation and natural differentiation. This has been demonstrated repeatedly for a variety of data sets from different regions and projects [8–10].

During the last 10–20 years several high-quality geochemical mapping projects with sample sizes in the vicinity of $n \sim 10^3$ have been carried out by geological

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survey organizations. The studied areas cover large regions up to whole continents and, despite their generally low sample densities, result in consistent and reproducible element distribution maps (e.g., [1, 11–17]). In the case of antimony, the distribution patterns resulting from these projects indicate a strong relation of antimony to geological units and natural processes such as weathering. Large-scale human impact would obliterate geological boundaries and overprint natural patterns with anthropogenic patterns like population density or industrial activity. Such effects of anthropogenic antimony input are not distinguishable at the continental scale. In contrast, a strong anthropogenic impact is clearly visible at local scales, for example, when mapping antimony in the surroundings of metal smelters, power plants, or in urban geochemical mapping projects (see [18] for examples).

To obtain a statistically based quantitative estimate of low levels of diffuse contamination we recently developed a method based on the comparison of the cumulative density functions (CDF) of top- and subsoil concentrations of an element on the regional to continental scale [19]. So far, results for lead [19], cadmium [20], and copper and zinc [21] have been presented. Modeled modifications of subsoil distributions in [19] demonstrate that the method can distinguish between influences of dilution or up-concentration, and the effects of diffuse, scattered, or local contamination, given a large enough data set of about 1,000 samples or more. Here the focus will be on studying the CDFs of antimony at the regional to continental scale for minerogenic (five examples from around the world with a focus on Europe) and organic topsoil (three examples from northern Europe). Furthermore, the GEMAS (geochemical mapping of agricultural soils) dataset [12, 22] will be used to visualize the regional distribution of antimony in agricultural (top)soil at the European scale.

6.2 Methods

6.2.1 Datasets

Table 6.1 summarizes information about and references to the datasets used. They cover continental to regional scales each using individually documented sampling and analytical procedures, and quality control results as referenced. For more details the reader is referred to the references provided. Results for antimony concentrations in three transects are included in Tabs. 6.1 and 6.2 to substantiate that a significant enrichment of antimony in organogenic topsoil is a general feature in northern Europe, and to provide a reference to data sources for antimony in plants, which are not discussed here.

Tab. 6.1: Overview of surveys and transects used. N: number of samples, size: area covered, DL: detection limit (mg kg^{-1}).

Survey scale and name	Material	N	size (km^2)	extraction	DL (mg/kg)	Reference
Continental scale (>1,000,000 km^2)						
Geochemical Survey of Australia	catchment outlet sediments, top and sub layer (0-10 & 60-80 cm)	1300	6.8 mill.	1:3 M HNO ₃ :HCl, ICP-MS	0.02	Caritat and Cooper, 2011a,b
North American Geochemical Landscapes Project	soil A and C horizon	4813/4780	c. 8 mill.	4-acid (total), ICP-MS	0.05	Smith et al., 2014
European FOREGS Project	top- and subsoil (0-25 & 50-75 cm)	783/840	4.4 mill.	4-acid (total), ICP-MS	0.02	Salminen et al., 2005
GEMAS Project	Ap (0-20 cm) and Gr (0-10 cm) soil	2108/2024	5.6 mill.	aqua regia, ICP-MS	0.02	Reimann et al., 2014a,b
The Baltic Soil Survey (BSS Project)	top- and subsoil (Ap and C horizon - 0-25 & 50-75 cm))	745	1.8 mill.	4-acid (total), ICP-MS	0.1	Reimann et al., 2003
Barents Project	soil O and C horizon	1337/1319	1.1 mill	4-acid (total), ICP-MS	0.02/0.01	Salminen et al., 2004
Regional scale (>10,000 but <1,000,000 km^2)						
Kola Project	soil O and C horizon	617/605	200.000	O: conc. HNO ₃ , ICP-MS; C: aqua regia, GFAAS	O: 0.01, C: 0.01	Reimann et al., 1998
North Trøndelag Project (NTR)	soil O and C horizon	752	25.000	aqua regia, ICP-MS	0.02	Reimann et al., 2015
Tellus Project, Ireland	top- and subsoil (5-20 & 35-50 cm)	6.862	14.000	aqua regia, ICP-MS	0.05	Young and Donald, 2013
Local scale (transects)						
			length (km)			
Oslo	bedrock, soil O and C horizon, 9 different plant materials	40	120	aqua regia, ICP-MS	0.02	Reimann et al., 2007
South Norway	soil O and C horizon, 4 different plants	44-46	200	aqua regia, ICP-MS	0.02	Reimann et al., 2009
Gjøvik	soil O and C horizon, 13	(36)- 41	100	aqua regia,	0.005	Flem et al., 2018;

Tab. 6.2: Analytical results (median values - *: estimated) for Sb from the projects named in the Methods section. The ratio between top- and subsoil is also provided. Information on sampling, analytical methods and detection limits is provided in Tab. 6.1.

ANTIMONY IN MINEROGENIC TOPSOIL				
Project	OHO mg/kg	Topsoil mg/kg	C (subsoil) mg/kg	O (Top)/C (Sub)
AUSTRALIA		0.12	0.13	0.92
USA		0.61	0.57	1.1
FOREGS (Europe)		0.6	0.47	1.3
FOREGS N-Europe		0.22	0.19	1.2
FOREGS S-Europe		0.88	0.83	1.1
GEMAS Europe		0.23		
GEMAS N-Europe		0.11		
GEMAS S-Europe		0.35		
BSS (N-Europe)		0.24	0.2	1.2
TELLUS		0.32	0.2	1.6
ANTIMONY IN ORGANOGENIC TOPSOIL				
Project	OHO mg/kg	Topsoil mg/kg	C (subsoil) mg/kg	O (Top)/C (Sub)
E-Barents	0.17		0.0024	7.2
Kola	0.183		0.009*	20
N-Trøndelag	0.33		0.04	8.2
Transects:				
Gjøvik	0.9		0.17	5.4
Oslo	1.235		0.165	7.5
S-Norway	1.38		0.07	21.2

6.2.2 Mapping

The obvious and central method for studying contamination is to create maps of the element concentration over the sampling area to detect anomalous patterns. Even though this appears to be a straightforward process, it requires some care to represent the relevant information. A most important imperative for an unbiased data analysis is to initially only map measured data and not interpretations, interpolations, or

predictions. A second rule is to choose the color scale in dependence of the data distribution, for example by using percentiles as color boundaries. The resulting maps can then be compared to geological, climatic, population, or other thematic maps to interpret conspicuous element distribution patterns.

6.2.3 CDF analysis

To distinguish background concentration variations from diffuse, scattered, and local contamination and to account for dilution or concentration processes that change the element concentration between different soil layers, it is helpful to represent the CDF of a data distribution in a cumulative probability (CP) plot. If topsoil and subsoil are chemically and mineralogically comparable, and neither weathering, nor biosphere processes, nor contamination considerably changes their chemical composition, then their CDFs should be almost identical. Accordingly, deviations between topsoil and subsoil CDFs can be used to infer information about the above-mentioned processes.

Successful CDF analysis requires a large dataset (> 500–1,000 samples) and low detection limits coupled with high analytical quality over the whole concentration range. Until quite recently, soil data sets from more than 500 samples for antimony have been scarce. Sufficiently low detection limits that resolve at least the full data distribution above the 5% percentile are still rare (for an example see Fig. 6.1). Another problem for elements with low concentrations in the sample material is that their CDFs are often obscured at the low-concentration end by discretization steps due to rounding to accuracy instead of precision. This is a routine procedure in many laboratories that unnecessarily renders valuable data practically useless.

In most environmental studies, like in mineral exploration, the interpretation is at present focused completely on the extremely high concentrations above the 95–98% percentiles of the measured CDF. If the survey area is not too large in comparison to the locus of contamination or mineralization, high element concentrations emitted from a defined source, like a metal smelter or a mineral deposit, can indeed distort the topsoil CDF in these upper concentration ranges. Examples of such massive metal contamination at the local to regional scale are the distributions of copper, cobalt, or nickel in the Kola region [1]. In exploration geochemistry, the upper percentiles of CP plots have been used since the early 1970s to identify unusual metal anomalies related to mineralization (e.g., [23, 24]). In contrast to massive local contamination, diffuse contamination is per se not expected to add exceptionally high element concentrations. Rather, it results in the initially low element concentrations at the lower percentiles of the CDF being raised by the added contamination that may be an insignificant fraction at high concentrations where it would not even be detectable.

Quite often a linear concentration shift (LCS) on the logarithmic scale between top- and subsoil is observed over the whole concentration range in these diagrams. A linear concentration shift by a factor a means that concentrations less than c in

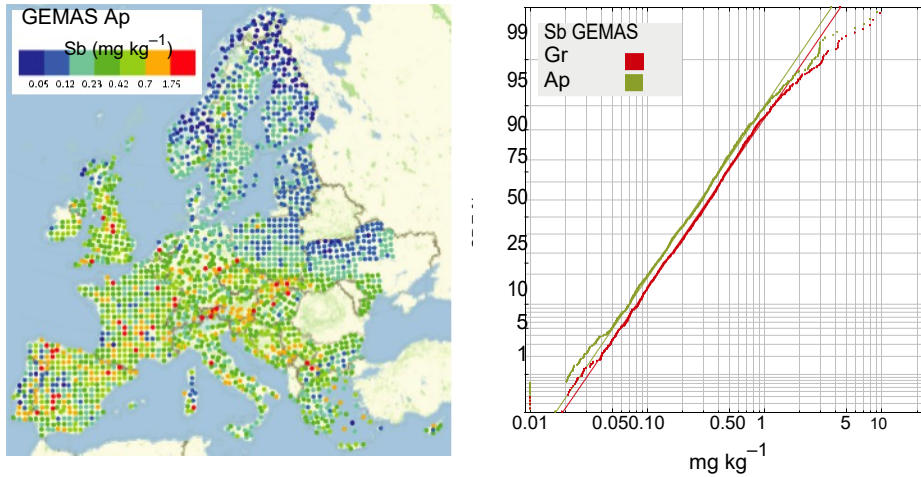


Fig. 6.1: Left: Sb distribution in European agricultural soil (A_p -layer, 0–20 cm). Right: CP plots of the Sb CDFs for agricultural (A_p , 0–20 cm) and grazing land (Gr, 0–10 cm) soil from the GEMAS project. Data from [12, 22].

the subsoil are equally abundant as concentrations less than $a \cdot c$ in the topsoil samples. This cannot be caused by contamination, but indicates a natural dilution or concentration process between the sample materials [19]. For some elements the LCS can be substantial when minerogenic subsoils are compared to organogenic (e.g., forest) topsoils. For some elements the LCS can be positive on the logarithmic scale, with $a > 1$, (e.g., silver, cadmium, mercury, and lead) or negative, with $0 < a < 1$, (e.g., Al), depending on the change in binding characteristics of the elements between the two matrix materials. The strong natural enrichment in the concentration of a number of elements in organic soils and coals has been recognized and described as early as 1937 [25].

Scattered contamination from spatially distributed localized emitters or sources – like smelters, power plants, or traffic – that raises element concentrations only at nearby sample locations is difficult to separate from diffuse contamination providing a blanket addition of element concentration from large-scale atmospheric transport and mixing processes that deposit an almost constant amount of contaminants at all sample sites. From the viewpoint of CDF analysis, the amount of ubiquitous diffuse contamination in a study area cannot be substantially higher than the minimum concentration found in the topsoil after correcting for the subsoil CDF through its LCS. Areas with unusual high concentrations in a survey area do not reflect diffuse contamination but outline local or scattered contamination, mineralization, or other element enrichment processes.

Unfortunately, diffuse contamination is only one process that shifts the lower end of the topsoil CDF toward “too high” concentrations. This shift can therefore be used only to estimate the maximal amount of diffuse contamination, because other

processes, like plants regulating the element concentrations in their organs, also can systematically enrich an element in the topsoil above a minimum level (e.g., cadmium [20]). Overabundant concentrations in topsoil become visible by overlaying the shifted subsoil and the topsoil CDFs [19]. They can occur at all concentration levels and may indicate scattered local contamination sources in the survey area or a strong climatic influence on element concentrations. The analysis of CDFs and CP plots is explained in more detail using example diagrams demonstrating the various effects, and applied to various elements, in [19–21].

6.3 Results

A percentile-based map of more than 2,000 individual measurements of antimony in European agricultural soil in Fig. 6.1 (data from GEMAS [12, 22]) dominantly features a clearly delineated step between concentration levels below the median in northern and correspondingly higher levels in southern Europe. This step coincides with the southern boundary of the last glaciation [12, 22]. The median antimony concentration in an aqua regia extraction is 0.35 mg kg^{-1} in southern Europe in contrast to 0.11 mg kg^{-1} in soils from northern Europe. The same trend is visible in Tab. 6.2: the projects from the far north of Europe (East Barents, Kola, and Nord Trøndelag project) report the lowest antimony median values in the C horizon. The fact that the GEMAS Sb map dominantly displays a geological boundary implies that the majority of antimony in European soils is of natural origin and demonstrates that the antimony background concentration range varies by a factor of more than 3 between northern Europe with a median of 0.11 mg kg^{-1} and southern Europe with a median of 0.35 mg kg^{-1} . The CP plot in Fig. 6.1 (right) demonstrates that it has become possible to produce high-quality antimony datasets with a sufficiently low detection limit to present practically the whole concentration range. Unfortunately, no subsoil was analyzed within the GEMAS project, as the focus was on agricultural (regularly ploughed) soil (0–20 cm, Ap samples) and grazing land soil (Gr).

FOREGS and GEMAS are two independent continental-scale geochemical mapping projects that collected independent soil samples at a low sample density (FOREGS: one site per $5,000 \text{ km}^2$, GEMAS: one site per $2,500 \text{ km}^2$) across the European continent. Because HF extraction was used in FOREGS, the median antimony concentration of 0.6 mg kg^{-1} for the FOREGS project is higher than the value of 0.23 mg kg^{-1} for the aqua regia extraction of the GEMAS project. Yet, the FOREGS and GEMAS projects report very similar antimony distribution patterns in European topsoil (see [14] or [18] for the FOREGS maps). This supports the validity and robustness of the low-density mapping approach [26]. It indicates that the antimony concentrations recovered in the two different extractions essentially reflect the same source material. This demonstrates that the low sample density is well suited for outlining the main processes

that determine the antimony distribution in soil at the continental scale, considering that the aim of a continental-scale geochemical mapping project is to achieve a general overview of the characteristic background variation in antimony, and not to detect new mineral deposits or to identify all local contamination sources, which are anyway usually known. By assuming that the soil surface expression of a local contamination source or a natural mineralization may cover only a very small area (for examples see [18]), the latter would require a sample density of around ten samples per km². Each of the approximately 2,500 cells with a size of 50 km × 50 km – which in GEMAS are represented by a single sample – otherwise would have to be covered by 25,000 samples. A corresponding European map would require consistent sampling and measurement of more than 60 million samples. These considerations emphasize that the similarity of independent low-density antimony maps is by no means self-evident but demonstrates the large-scale nature of variations in antimony background concentrations. This is also true for the internal comparison of the independent GEMAS agricultural soil (Ap) vs. GEMAS grazing land soil (Gr) samples.

Table 6.2 highlights several general features of antimony values as observed in soil:

- 1) There are substantial differences between the results obtained for aqua regia and near-total 4-acid (including HF) extraction. The median value for aqua regia soluble Sb in European topsoil is by almost a factor 3 lower in the GEMAS project than in the FOREGS project that used the stronger extraction.
- 2) For minerogenic soils antimony is generally enriched by a factor of 1.1 to 1.6 in topsoil. This appears to be independent of the extraction and the soil type sampled. The only exception are the Australian soils, where the antimony median value is somewhat lower in topsoil that may be related to winnowing of fines.
- 3) Antimony median concentrations are quite comparable for minerogenic and organogenic topsoil – this is surprising given the large difference between the two sample materials; the forest soil O horizon consists of decaying plant material. Plants do in general not tend to substantially take up or enrich antimony [18, 27, 28].
- 4) The ratio between topsoil and bottom soil is much larger in the projects that used an organic topsoil (forest soil O horizon). When organic topsoil was collected this ratio is between 5 and 20. Unfortunately all projects using organogenic topsoil were carried out in northern Europe, where the antimony concentrations in the C horizon are in general much lower than in southern Europe (Tab. 6.2).
- 5) Antimony concentrations are much higher in the older and more weathered soil of southern Europe, than in the young (<10,000 years) and much less weathered soil of northern Europe. The difference is almost a factor 3.

The median values for northern Europe (BSS project and FOREGS northern Europe – Tab. 6.2) both using a strong extraction, including HF (Tab. 6.1), are almost identical, although these are two completely independent surveys with independent sample locations.

When studying the CP diagrams for the different projects with a sufficiently large sample number (Figs. 6.2 and 6.3) it becomes clear that there still exist many problems with regard to reliable antimony analyses.

In many projects the detection limit is too high to get a reliable expression of the statistical distribution in the low concentration range. For the Australian data set about 7% of the samples returned values below detection in both layers. In addition, the effects of unnecessary data rounding by the laboratory are clearly visible and affect the data distribution from about the 80th percentile downward. Artificial steps due to rounding are also visible for the FOREGS dataset from the 30th percentile downward. For the Baltic Soil Survey (BSS) more than 10% of all topsoil and subsoil samples returned values below detection. The Tellus samples are again affected by excessive rounding down from about the 75th percentile. For the East Barents Project

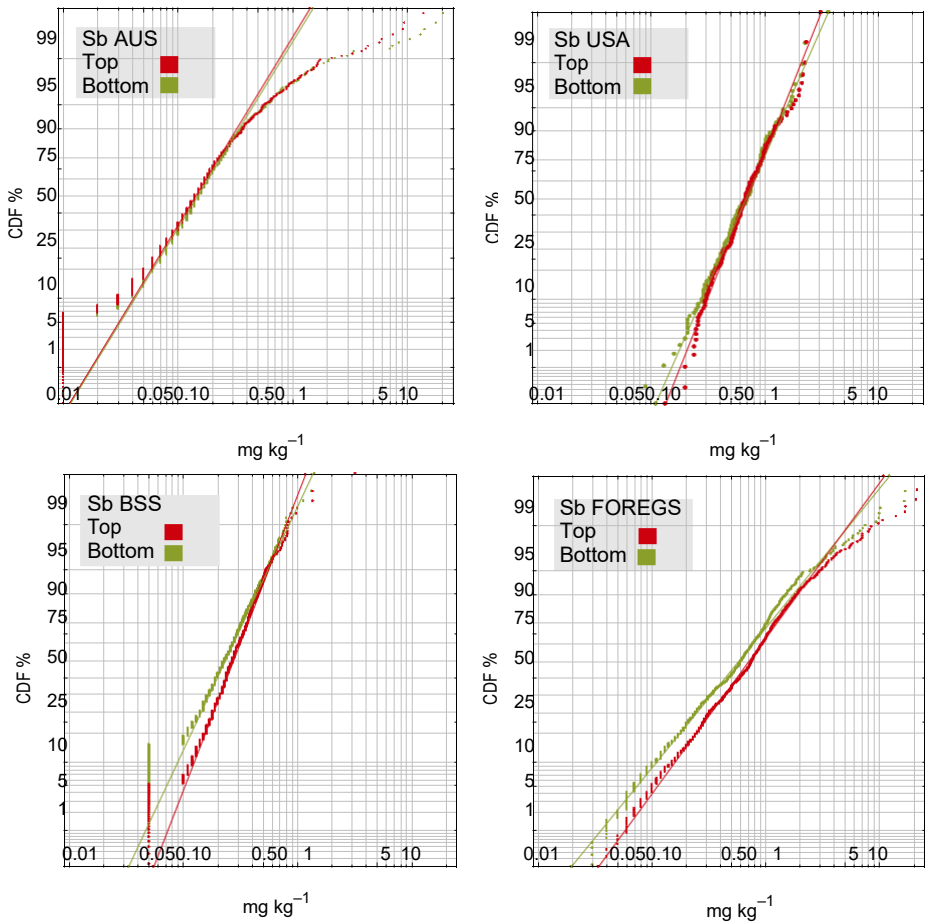


Fig. 6.2: Four CP diagrams for projects using minerogenic topsoil (Australia, USA, FOREGS and BSS projects).

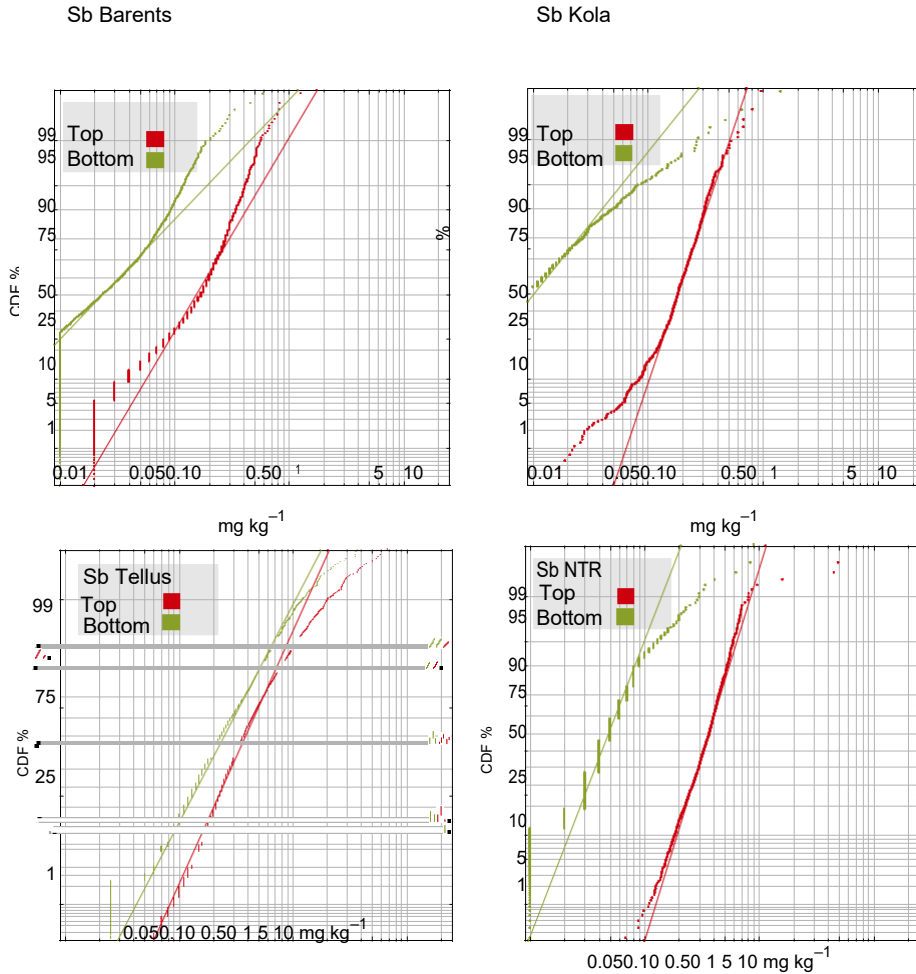


Fig. 6.3: Four additional CP diagrams: Tellus used minerogenic topsoil, and E-Barents, Kola and Nord Trøndelag (NTR) projects used organogenic topsoil.

25% of the C horizon and about 6% of the O horizon samples are below detection and the O horizon samples are severely affected by excessive rounding. For the Kola project about 50% of the C horizon samples are below the detection limit. For the Nord Trøndelag Project, again the C horizon samples are severely affected by a high detection limit and by excessive rounding of over 90% of the C horizon results. All three projects using organogenic topsoil show unusually low antimony concentrations in the subsoil (C horizon). This is probably due to weathering and the history of soil formation (see difference between northern and southern Europe in Fig. 6.1). The bed-rock may also play a role as large areas of northern Europe are covered by Archaean to Proterozoic crystalline rocks. Unfortunately, a good litho-geochemistry database providing total antimony concentrations for different bedrock types and ages is still missing.

To better estimate diffuse antimony contamination it would be especially important to obtain reliable antimony concentration data with low detection limit and better resolution. This precision at low values is needed because samples with low natural antimony concentration are most affected by diffuse input across Europe [19]. In so far, it is surprising that the estimates for excess antimony, and LCS values still lead to quite coherent values for all data sets.

The CDFs for the BSS and Tellus projects exemplarily demonstrate the effect that one would expect to see for diffuse contamination [19]: a slightly increased concentration steepens the CDF of the top layer at the lower concentration range, but due to the logarithmic scale almost disappears toward higher concentrations. For the surveys using minerogenic topsoil only a small linear concentration shift is visible (up to 1.39 – Tellus). Excess antimony ranges between 0 (Australia) and 0.054 mg kg^{-1} (BSS, northern Europe). The excess antimony for Europe (FOREGS) is 0.03 mg kg^{-1} . This on a first glance low value – which corresponds to the median excess antimony value for minerogenic soil – still represents about 10% of the median antimony concentration in European minerogenic topsoil, which would actually be a quite substantial fraction if it originates from anthropogenic input (Tabs. 6.2 and 6.3). The highest values of excess antimony in minerogenic soil are observed for the Tellus and BSS projects (Tab. 6.3). These are exactly those projects where at least some of the topsoil samples contain more organic material than usual due to wet and cold climatic conditions that favor the accumulation of organic material in soil. Thus the observed “excess” is probably not exclusively due to diffuse contamination, but will also reflect a constant addition of antimony due to a constant amount of more antimony-rich organic material in the soil samples from these surveys.

The three projects using organogenic topsoil (the forest O horizon) show quite different results: linear concentration shifts of 2.59 (E-Barents) to 4.52 (Nord Trøndelag) reflect the much lower antimony concentrations observed in the C horizons in northern Europe (Tab. 6.2). The median value for excess antimony is now 0.13 mg kg^{-1} compared to the 0.03 mg kg^{-1} reported for minerogenic topsoil. The three projects that use organogenic topsoil (see Tab. 6.2) deliver estimates of excess antimony in a narrow range from 0.1 mg kg^{-1} (E-Barents) to 0.18 mg kg^{-1} (Kola). In this case the excess antimony, besides diffuse contamination, also may reflect biologically adjusted antimony levels through plant interactions, strong organic binding, or climatic effects. Unfortunately, the statistical interpretation based on CDF analysis of the available data cannot differentiate between these processes. Thus the estimate of 0.03 mg kg^{-1} from the projects with minerogenic topsoil provides the most reliable estimate of maximum input of antimony via diffuse anthropogenic contamination at the European scale. The value obtained for the United States, 0.024 mg kg^{-1} , is quite comparable (see Tab. 6.3). In Australia no excess antimony is visible.

The CDF of the O horizon for the Kola Project indicates that there are too many high antimony values in the middle concentration range in the O horizon. This appears to be a climatic effect. Increased bioproductivity from the coast of the Barents

Tab. 6.3: Excess Sb (in mg kg^{-1}) and linear concentration shift (LCS) for eight regional to continental-scale projects. CvM refers to the p-value of the Cramer-von Mises test [31]. CvM-values larger 0.05 indicate that the hypothesis that the adapted subsoil Sb distribution agrees with the topsoil distribution cannot be rejected on a 5% level (see [19]).

MINEROGENIC TOPSOIL			
Project	excess Sb mg/kg	LCS	CvM
AUSTRALIA	0.0	1.0	0.07
USA	0.024	1.0	0.27
FOREGS (Europe)	0.03	1.19	0.84
BSS (N-Europe)	0.054	0.934	0.11
TELLUS	0.048	1.39	0.008

ORGANOGENIC TOPSOIL			
Project	excess Sb mg/kg	LCS	CvM
E-Barents	0.10	2.59	0
Kola	0.18	2.88	0
N-Trøndelag	0.13	4.52	0.0003

Sea toward the south leads to a strong north-south gradient in antimony concentrations in the O horizon [18, 29]. While in the O horizon the lowest antimony concentrations occur along the coast, the highest antimony concentrations in the C horizon mark the Caledonian sediments occurring along the coast [1].

A constant diffuse input of antimony to European soil is thus in the range of 0.01 mg kg^{-1} to 0.05 mg kg^{-1} with a most likely value of $<0.03 \text{ mg kg}^{-1}$. The EU risk assessment report for Diantimony trioxide [30] provides a predicted no effect concentration (PNEC) of 37 mg kg^{-1} dry weight for soil. This value is by three orders of magnitude higher than the observed diffuse input at the continental scale. Because no adverse effect is expected from these low concentrations, it appears justified to conclude that there is no “diffuse pollution” by antimony in soil, although up to 10% of the soil median antimony content may be due to diffuse contamination. True antimony pollution will be observed – and needs to be abated – at the local scale, for example, near metal mines or smelters, and in some extreme cases at urban pollution hotspots (see [18]), which all require mapping at the local scale.

6.4 Conclusions

Large-scale regional to continental-scale surveys of antimony concentration in soils provide a consistent and important view on antimony distribution and indicate possible origin and transport processes. Statistical analysis of topsoil versus subsoil concentrations permits estimation of a maximal amount of diffuse antimony contamination in topsoil. The main results can be summarized as follows:

- (a) Reported antimony concentrations strongly depend on the chemical extraction method employed. For GEMAS, using aqua regia, the median of 0.23 mg kg^{-1} is by a factor 3 smaller than for a near total 4-acid extraction, including HF as used in the FOREGS project (median 0.6 mg kg^{-1}).
- (b) Improvements in analytical quality would considerably help to achieve a more detailed overview of the distribution of antimony in soil, which at present is still hampered by too high detection limits and excessive and usually unnecessarily strict rounding of the reported results by many laboratories.
- (c) In Europe a strong difference in antimony concentration is observed between southern (high Sb) and northern Europe (low Sb). The FOREGS project shows a factor 4 difference in the median concentration for southern Europe (0.88 mg kg^{-1}) when compared to northern Europe (0.22 mg kg^{-1}). For the GEMAS project the median for southern Europe is 0.35 mg kg^{-1} and that for northern Europe is 0.11 mg kg^{-1} , a factor of 3 lower. In a European map of antimony in agricultural soil, the concentration break between southern and northern Europe follows the southern border of the last glaciation. This may relate to lithological differences between older crystalline rocks in the north and their weathering products moved south by glaciation, and younger sedimentary rocks and volcanics, in the South. More likely, this antimony concentration difference reflects the huge difference in soil age and thus in weathering. A larger fraction of the total antimony in the older and more weathered soils in southern Europe has been released over time and is accessible to acid extraction.
- (d) Median antimony concentrations in topsoils are quite comparable for both minerogenic and organogenic topsoil (the forest soil O horizon). Within the surveys covering northern Europe (0.20 vs. 0.18 mg kg^{-1}) the projects based on organogenic topsoil show a much larger difference between topsoil and subsoil. The ratio of topsoil/subsoil antimony concentrations is close to 1 when minerogenic topsoil is collected and reaches values of 5 to 20 for the projects where organogenic topsoil was collected. This is also reflected in a substantial linear concentration shift visible for these projects. Excess antimony in organic topsoil is in consequence also by almost an order of magnitude higher than observed for the projects collecting minerogenic topsoil.
- (e) Notwithstanding the many uncertainties and the limited data quality for antimony concentrations in most projects, it is possible to estimate the maximum amount of diffuse antimony contamination in the European soil samples. Not more

than 0.03 mg kg^{-1} antimony can be due to diffuse contamination. In some respect, this is a rather high value, as it corresponds to about 10% of the median antimony concentration. On the other hand, it is small enough to explain why the patterns observed in continental-scale maps of antimony in soil from three continents (BSS, FOREGS, GEMAS, USGS geochemical landscapes, and geochemical atlas of Australia), as well as the maps from more regional scale projects (Kola, Nord Trøndelag, Tellus), are clearly dominated by natural processes. Local contamination or the occurrence of mines is sometimes marked by local anomalies.

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