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Estimates of ambient background concentrations of trace metals in soils for risk assessment

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Ambient background concentrations of Cd, Co, Cr, Cu, Ni, Pb and Zn in surface soils are estimated using the soil inventory data for England and Wales.

Abstract

Site-specific or soil type-specific ambient background concentrations (ABCs) of trace metals in soils are needed for risk assessment. We investigated three different methods for estimating ABCs in soils using a dataset of 5691 soil samples from England and Wales. The concentrations of Co, Cr and Ni were strongly associated with Al and Fe, and multiple regressions explained 62–85% of their variation, and Al and Fe can therefore be used to predict ABCs for these metals. Soil texture had a major influence on the concentrations of Cd, Co, Cr, Cu, Ni and Zn, and the medians were 3–5 fold higher in clayey than in sandy soils. This was used to predict texture-specific ABCs. Lead concentration was higher in acidic peaty soils than in other soils. A probability graph method was used to estimate ABC for Pb in a population of relatively uncontaminated soils. Potential applications of ABCs are discussed.

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Keywords: Ambient background concentration; Trace metals; Soils; Risk assessment

1. Introduction

Trace metals in surface soils are derived from both parent materials and anthropogenic activities. Because of the latter, it is often difficult to quantify the natural background concentrations of metals in soils. In fact, it can be argued that natural background no longer exists on this planet because of human influence (Reimann and Garrett, 2005), and this is particularly true for long-industrialised regions like the UK. Therefore, the usual, or ambient, concentration of a metal in soil consists of both a natural pedo-geochemical fraction and an anthropogenic fraction (International Organisation for Standardisation (ISO), 2005). In the ISO document, the anthropogenic fraction refers to moderate diffuse inputs into the soil, not the inputs

from local point sources that generally result in a much elevated concentration. In this paper, we have used the term “ambient background concentration” (ABC) with the same meaning as that of “usual background concentration” defined by ISO.

ABCs of trace metals in soils may vary depending on soil types and land uses. Soil parent materials and pedogenesis clearly have a key influence on metal ABCs (Palumbo et al., 2000; Baize and Sterckeman, 2001; Rawlins et al., 2003). Attempts to define a single background value, or an ABC, for a large area is fraught with problems because of heterogeneity of regional geochemistry and the fact that ABC is a range, not a single value (Reimann and Garrett, 2005). Use of a single ABC for a large area, regardless of the spatial variation in soil type and properties, could give rise to either overestimation or underestimation of metal contamination and the associated risk for a particular soil. The question arises whether it is possible to estimate a local or soil-type

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specific ABC, which is essential for risk assessment and regulation of metals in soil.

There is as yet no agreed method for the estimation of a local or soil-type specific ABC. Kabata-Pendias et al. (1992) suggested that mean values and ranges of trace metal concentrations in soil taxonomical units calculated from existing databases seem to provide acceptable background values and can serve for the assessment of changes at the local and regional scales. However, their study showed that the differentiation in metal concentrations among soil taxonomical units was not as clear as among soil textural classes, and that the mean and range of a trace metal for the same taxonomical unit varied considerably among different central-eastern European countries. Furthermore, use of mean values is not statistically justified because soil geochemical data rarely show a normal distribution, but are often positively skewed, even after logarithmic transformation (Reimann and Filzmoser, 2000). More appropriately, ABCs should be set at a chosen parameter (e.g. median or 90th percentile) from the frequency distribution of the ambient concentrations of trace metals (International Organisation for Standardisation (ISO), 2005). This method requires a sufficiently large dataset generated from soil geochemical survey conducted at a local regional scale, and can be enhanced when information of soil type, texture, parent material and land use is also available.

Another method is to take metal concentrations measured in the deeper soil horizon (e.g. the C horizon) as the local background for the top soil, usually after correction for the variation of a reference element such as Zr (e.g. Blaser et al., 2000). This method, named the enrichment factor approach, has been criticised for, among other things, failing to take into account the natural biogeochemical processes that redistribute elements in the soil profile (Reimann and de Caritat, 2005; Reimann and Garrett, 2005).

The third approach uses the relationships between trace elements and semi-conservative elements such as Fe, Al and Mn to predict the expected values of trace elements in top soils. Hamon et al. (2004) analysed soil geochemical data in Namibia, Australia and Asia and used relationships with Fe or Mn to make estimates of the background concentrations of As, Co, Cr, Cu, Ni, Pb and Zn, assuming that the soils in a sub-set from “remote areas” were uncontaminated. Their study showed that the relationships are remarkably independent of both soil type and climatic setting, and the “background” concentrations of trace elements can vary by more than an order of magnitude. Sterckeman et al. (2006) also used a similar approach to estimate the “pedo-geochemical background” concentration of a range of trace elements in soils developed from loess deposit in northern France.

In this paper, we present results from statistical analyses of the soil geochemical data for England and Wales (the National Soil Inventory, NSI), with the aim of estimating local or soil-type specific ABCs for the trace elements Cd, Co, Cr, Cu, Ni, Pb and Zn. We also explored the probability graph method (Sinclair, 1974; Davies, 1983) as a way for estimating average regional ABCs for metals in the soils of England and Wales. Potential uses of ABCs are then discussed.

2. Materials and methods

2.1. Data

The data used in the present study are from the National Soil Inventory (NSI) of England and Wales. A total of 5691 soils (0–15 cm) were sampled from the intersects of 5-km orthogonal grids between 1978 and 1983. The sampling was therefore unbiased, and not targeted at any particular land use, and included all types of land use. No attempt was made to devise a sampling strategy to cover urban areas adequately, so the coverage is predominantly non-urban. A wide range of physical and chemical properties were determined in the soil samples. Details of sample collection and preparation, analytical methods and quality control, summary statistics and maps for many of the measured soil properties were published in the Soil Geochemical Atlas of England and Wales (McGrath and Loveland, 1992). A further project looked at the detailed spatial relationships within the NSI data (the geostatistics), and the application to the design of a soil monitoring network for England and Wales (Oliver et al., 2002).

All soils were analyzed for Al, Ba, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, P, K, Na, Sr and Zn. The focus of this study is on seven trace metals Cd, Co, Cr, Cu, Ni, Pb and Zn. The elemental concentrations were those determined following aqua regia digestion (McGrath and Cunliffe, 1985), which are often referred to as pseudo-total concentrations. Certified reference soils from the BCR (Community Bureau of Reference) were used for quality control as these had certified results for the concentrations of metals in aqua regia digests. The detection limits (calculated as 5 times the absolute instrumental detection limits) were 0.2, 0.5, 1.0, 0.75, 2.0, 4.7 and 0.7 mg kg⁻¹ for Cd, Co, Cr, Cu, Ni, Pb and Zn, respectively. There are 5651 data points for pH and organic C, and 4842 data points for clay content. Clay content was not determined in peaty soils (generally with organic C > 12%). Soil pH was determined in water (soil:water 1:2.5). Organic C was determined either by a dichromate digestion method for soils containing <20% C, or by loss-on-ignition for soils containing >20% (McGrath and Loveland, 1992). The information of soil texture, classified according to Avery (1980), was available from field assessments carried out at the time of soil sampling. There were six texture groups plus a group of peaty soils, with each texture group consisting of various texture classes (Table 1). Additionally, the major soil taxonomical group was recorded for each sample. There were ten major taxonomical groups for the soils in the NSI dataset, and their approximate equivalents in the USA and FAO classification systems were described by McGrath and Loveland (1992).

2.2. Statistical analysis

In the dataset, the distributions of the concentrations of the seven trace metals were positively skewed, as is often found with geochemical data (McGrath and Loveland, 1992; Reimann and Filzmoser, 2000). A log₁₀ transformation reduced the skewness and kurtosis substantially. However, even this transformation did not produce normally distributed data. Box plot analysis was performed for the Cd, Co, Cr, Cu, Ni, Pb and Zn data, based on both untransformed and log₁₀-transformed values. This analysis identifies the median, the values for the 25th and 75th percentile, and the upper and lower whisker

Table 1
Groups and classes of soil texture from field assessment^a

Texture group	Class
Sandy	Coarse sand, loamy coarse sand, medium sand, loamy medium sand, fine sand, loamy fine sand
Coarse loamy	Sandy loam, sandy silt loam
Fine loamy	Sandy clay loam, clay loam
Coarse silty	Silt loam
Fine silty	Silty clay loam
Clayey	Sandy clay, silty clay, clay
Peaty	Peaty

^a Classification of soil texture was according to Avery (1980).

(Tukey, 1977). The lower and upper whiskers are 1.5 times the inter-quartile range. Correlation analysis was done on the \log_{10} -transformed data (except clay content, which showed a normal distribution without transformation). Next, principal component analysis (PCA) was performed on the correlation matrix to provide an overall view of the relationships among variables. For PCA, a dataset including all elemental concentrations, organic C and pH was used. Clay content was not included in the PCA because otherwise most of the peaty soils would have been excluded in the analysis due to the lack of clay data. Metal concentrations below the detection limits were taken as they were in the database in the box plot and PCA analyses, except 74 data with zero Cd, which could not be log transformed. These 74 data were excluded whenever $\log_{10}\text{Cd}$ was used in statistical analysis.

Simple or multiple linear regression analysis was performed on the \log_{10} -transformed data of Al, Fe and the seven trace metals. Here we made a decision to exclude those data that were below the detection limits or outliers above an upper limit (upper outliers). According to the EU Technical Guidance Document (TGD) for risk assessment (European Commission, 2003), data that are used for assessing environmental concentrations in the regional scenario should not be influenced directly by point-source emissions. The TGD recommends that the upper whisker for the \log_{10} -transformed data be taken as the cut-off level for the upper outliers, if the dataset is sufficiently large. Thus, the upper outliers are defined as:

$$\log_{10}(x_i) > \log_{10}(p75) + 1.5 [\log_{10}(p75) - \log_{10}(p25)]$$

where x_i is the outlier cut-off value, $p25$ and $p75$ the 25th and 75th percentile of the distribution. For Co, Cr and Ni, for which regression analysis was applied (see below), only very small numbers of samples were excluded because they were either below their respective detection limits (0.2–1.1% of the dataset) or above the outlier cut-off values (0.2–0.5% of the dataset). Exclusion of these data points benefited regression analysis because of a considerable reduction of skewness and kurtosis.

2.3. Frequency distribution according to texture groups

For the seven trace metals, analysis of variance (ANOVA) was performed on the \log_{10} -transformed data to test the significance of the influence of soil texture group or major taxonomical group. ANOVA identified soil texture as a key soil factor influencing trace metal concentrations. The data were then sorted according to the seven texture groups (Table 1). The number of samples varied from 182 for the coarse silty group to 2002 for the fine loamy group. Frequency distributions of the concentrations of the seven trace metals within each texture group could not be fitted satisfactorily with parametric distribution functions (e.g. normal, log-normal, gamma, or Weibull). Therefore, non-parametric distributions were used. Data were ranked in ascending order, and the cumulative probability of a data point x_i was calculated according to the following formula (Cullen and Frey, 1999):

$$F(x_i) = (i - 0.5)/n$$

Where i is for the rank order of the sorted data and n is the total number of data points within each texture group. Median and percentile values were obtained from this empirical distribution function. All data, including those below the detection limits and zero Cd values, were used in this analysis.

All statistical analyses were carried out using Genstat version 8.2 (VSN International Ltd, Hemel Hempstead, UK).

2.4. Probability plots

Probability graph paper has been used by geochemists to determine the threshold or ‘inflection point’ between anomalously high and background geochemical data, with the aim of mineral prospecting (Sinclair, 1974). However, Davies (1983) applied this method in a different way. He used the method to estimate the mean and the range of Pb concentrations that are likely to be associated with uncontaminated soils, using survey data from four areas in England and Wales. In this method, \log_{10} -transformed soil metal concentrations (y -axis) are plotted against their cumulative frequency distributions on the probability scale (x -axis). A straight line means that the data

are log-normally distributed, which is usually considered to be the case if all data points are from a single population of samples. However, because a country-wide or regional survey may cover soil samples belonging to both uncontaminated and contaminated populations, the relationship between \log_{10} metal concentration and cumulative frequency presented on a probability graph is more likely to be a curve. Mixed populations may also be present, giving rise to curves with inflexion points related to the proportion of each population present. The linear portion associated with low metal concentrations is taken as representing the distribution of the uncontaminated soils (Davies, 1983). Here, ‘uncontaminated’ soils should be taken as those not impacted by point-source contamination, rather than pristine soils. More details of the method were given by Sinclair (1974) and Davies (1983). We applied the method to derive geometric mean and the 10th–90th percentile range for seven trace metals in the ‘uncontaminated’ population within the NSI dataset, although a detailed examination showed that this approach was not suitable for metals other than Pb.

3. Results and discussion

Concentrations of all seven metals in soils varied widely. Fig. 1 shows the box plots for the log-transformed data of Cd, Co, Cr, Cu, Ni, Pb and Zn.

3.1. Principal component analysis

PCA identified four principal axes with latent roots of 9.1, 2.7, 2.1 and 1.0, accounting for 47.9%, 14.4%, 10.8% and 5.3% (or 78.4% in total) of the total variance, respectively. The latent vectors describe the contribution to the variation of each variable on each of the principal axes. The larger the absolute values of the latent vectors, the greater the proportion of the variation a particular variable accounts for on

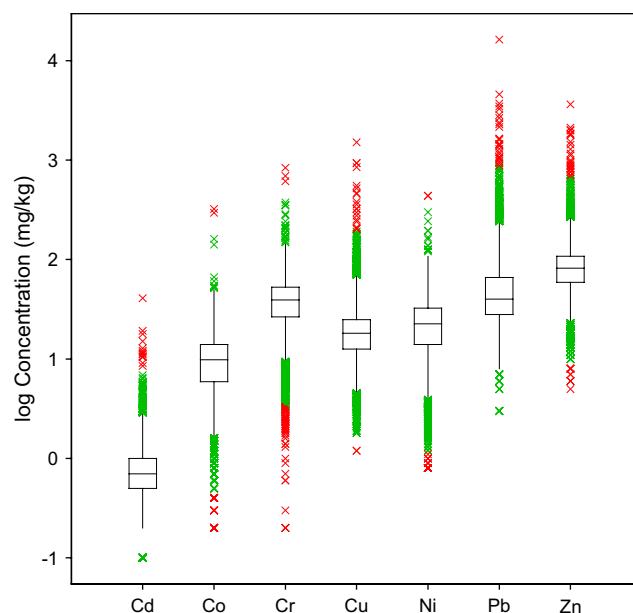


Fig. 1. Box plots for the log-transformed data of Cd, Co, Cr, Cu, Ni, Pb and Zn. The rectangular box represents 25th–75th percentile range (hinge width), the horizontal line inside the box the median, vertical lines outside the box are lower and upper whisker (each being 1.5 times the hinge width). Outliers and far outliers are shown as green and red crosses, respectively. Outliers and far outliers are defined as values beyond 1.5 or 3 times the hinge width outside the central inter-quartile box, respectively.

a given axis. For the first principal axis, Al, Fe, Co, Cr, Ni, K and Mg had latent vector values greater than 0.25 (in absolute value), suggesting that this component represents variation in the structural elements of soil minerals (Al, Fe and K) and the metals associated them. The second principal component was dominated by organic C, Pb, Cu and pH (latent vector absolute values >0.25), suggesting the influence of acidic peaty soils and the association of Pb and Cu with these soils. The variables with latent vector values >0.25 for principal component 3 included Ca, Sr, pH and P, suggesting that this component represents variation in acidity and possibly also the influence of agricultural practices. The concentration of Na had a particularly large value of latent vector (0.65) in principal component 4, suggesting that this might represent a marine influence.

The latent vector loadings for the first three principal components are shown in Fig. 2. This clearly shows the association among Al, Fe, K, Mn, Cr, Co and Ni. This association can be explained by classical geochemistry. For example, Co and Ni are classified as siderophilic (iron-loving), and trivalent forms of Cr, Fe and Al also tend to associate with each other (Goldschmidt, 1954). Similarly, Sterckeman et al. (2006) reported a close association between Co, Cr and Ni with Al and Fe in a survey of 52 surface soils from northern France. Other associations include Zn and Cd, which often occur together in minerals. The association among Ca, Sr and pH is easily understood because of their relationship with acidity. Fig. 2 confirms the tendency for Pb and organic C to be associated with each other, due to the generally large Pb concentrations in upland peaty soils in northern and western England, where there is a long history of Pb mining and smelting, and the fallout of Pb from the atmosphere to acid ombrotrophic peat may be further enhanced by high rainfall (McGrath and Loveland, 1992).

3.2. ABCs for Co, Cr and Ni derived from regression analysis

Informed by the results from PCA, we performed regression analysis between Co, Cr, Ni and Fe or Al. Aqua regia-soluble Fe and Al can be considered as semi-conservative properties of soils; their concentrations are related more to the chemical composition of the soil-forming parent materials and the degree of weathering than to the anthropogenic influence (Hamon et al., 2004). Unlike Hamon et al. (2004), we found only weak associations between Zn, Cd, Cu or Pb and Fe (or Al, Mn) (Fig. 2). This, and the strong relationship between Co, Cr, Ni and Fe or Al, are both in accord with classic geochemistry (Goldschmidt, 1954). Therefore, regression was only performed between the latter group of elements.

Coefficients for simple regressions between Co, Cr or Ni and Al or Fe are presented in Table 2. These regressions explained 53–72% of the variation in the trace metal concentrations, which is considered to be satisfactory for such a large dataset. Fig. 3 shows an example for the relationships between Co and Al or Fe. Note that most of the data points actually lie in the dark areas close to the regression lines on Fig. 3. The relationships for Cr were better, and for Ni slightly poorer (graphs not shown) than for Co. Linear regression based on log₁₀-transformed data is appropriate because no non-linear trends were observed in the relationships (Fig. 3) and the distribution of residuals (not shown) is considered to be acceptable for such a large dataset. Regression with Al was better than with Fe for Cr; the opposite was true for Co and Ni (Table 2).

For all three trace metals, a multiple regression including both Al and Fe as independent variables improved the model fit, resulting in a decreased standard error of observation and increased the percentage of variance accounted for (R^2_{adj}) to 71%, 85% and 62% for Co, Cr and Ni, respectively

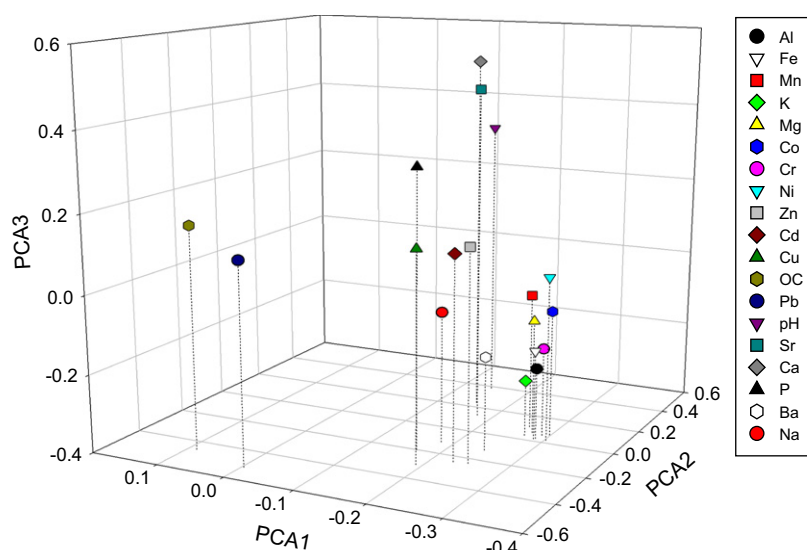


Fig. 2. Latent vector loadings for 19 variables used in principal component analysis. PCA 1, 2 and 3 accounts for 47.9, 14.4 and 10.8 of the total variance, respectively.

Table 2
Coefficients for regression equations relating Co, Cr or Ni to Al and/or Fe

Dependent variable (y)	Independent variable (x)	Regression coefficients			n	R ² _{adj}	SE of observation
		Constant	Slope (x ₁)	Slope (x ₂)			
log ₁₀ Co	log ₁₀ Al	-3.15 ± 0.048	0.93 ± 0.011		5623	0.56	0.226
	log ₁₀ Fe	-3.72 ± 0.041	1.06 ± 0.0094		5623	0.69	0.188
	log ₁₀ Al (x ₁), log ₁₀ Fe(x ₂)	-3.92 ± 0.042	0.26 ± 0.015	0.84 ± 0.016	5623	0.71	0.183
log ₁₀ Cr	log ₁₀ Al	-2.37 ± 0.025	0.89 ± 0.0056		5653	0.82	0.121
	log ₁₀ Fe	-2.20 ± 0.031	0.85 ± 0.0071		5653	0.72	0.149
	log ₁₀ Al (x ₁), log ₁₀ Fe(x ₂)	-2.64 ± 0.024	0.63 ± 0.0090	0.33 ± 0.0092	5653	0.85	0.109
log ₁₀ Ni	log ₁₀ Al	-2.13 ± 0.043	0.78 ± 0.0099		5612	0.53	0.199
	log ₁₀ Fe	-2.35 ± 0.041	0.83 ± 0.0094		5612	0.58	0.187
	log ₁₀ Al (x ₁), log ₁₀ Fe(x ₂)	-2.63 ± 0.041	0.35 ± 0.015	0.55 ± 0.015	5612	0.62	0.179

Concentrations of all elements are in mg kg⁻¹.

(Table 2). Therefore, we recommend that the multiple regression equations be used in the prediction of ABCs of Co, Cr and Ni in topsoils.

The approach of Hamon et al. (2004) was slightly different. They removed the upper 5% data points which gave rise to the largest positive residuals from the regression line, and derived the line encompassing the upper 95th percentile of the data, which was then used to predict the background metal concentrations. In this case, the predicted background concentrations are in fact the 95th percentile values, which would be

considerably larger than the mean values calculated from the regression equations presented in Table 2. One potential weakness in the approach of Hamon et al. (2004) is that the poorer the relationship between a trace metal and Fe or Al concentrations, the larger the predicted background concentration for the trace metal. Deriving a larger soil background because of a poor fit is not a conservative approach and may lead to under-protection of soil from metal pollution.

Similarly, Sterckeman et al. (2006) used the relationships between trace elements and Fe or Al concentrations in 52 surface soils developed from loess deposits in northern France to predict the “pedo-geochemical background concentrations” of the former. Regression equations were presented for a range of trace elements including As, Bi, Cu, Mo, Pb, Sb, Sn, Tl, V and Zn, although the R² values were low (<0.5) for several of them. It is arguable whether the values are true pedo-geochemical background concentrations, because the fractions of anthropogenic-derived trace metals could not be excluded prior to the regression analysis. For this reason, as here, ambient background concentration (ABC) would be a more appropriate term.

3.3. ABCs of trace metals in soils according to texture group

The regression approach described above was not found to be appropriate for other trace metals like Cd, Cu, Pb and Zn, because of the lack of a close relationship with Al or Fe. Analysis of variance based on log-transformed data shows that both soil texture and major soil taxonomical group have a highly significant influence on the concentrations of the seven trace elements. Soil texture explains the variation in trace metal concentration better (percentage of variance accounted for 10.2–46.3%) than major soil taxonomical group (3.6–21.9%) (Table 3). McGrath and Loveland (1992) and Kabata-Pendias et al. (1992) showed that the distribution of trace metals (Mn, Cr, Cu, Ni and Zn) among soil textural classes is differentiated more strongly than among soil taxonomic units. Baize (1997) also found that the concentrations of eight trace elements differentiated strongly among soil texture

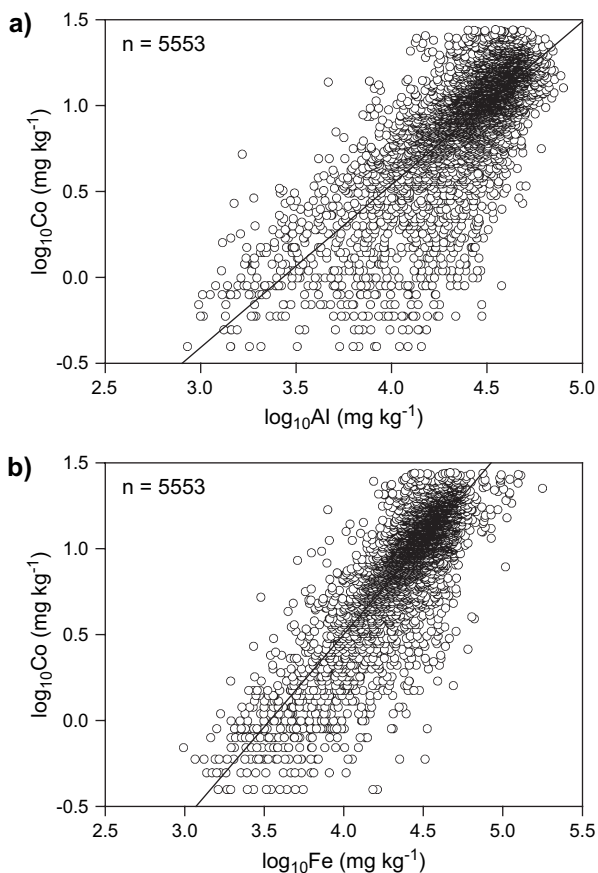


Fig. 3. Relationships between Co and Al (a) or Fe (b).

Table 3
Influence of soil texture and major taxonomical group on trace metal concentrations

Trace metal	Soil texture	Soil group
Cd	27.8	3.6
Co	43.2	20.8
Cr	46.3	21.9
Cu	10.2	3.6
Ni	40.3	19.7
Pb	17.4	10.2
Zn	20.0	6.7

The values are % of variance accounted for by soil texture or taxonomical group.

classes in 580 French soils. There is a clear tendency for metal concentrations to increase from light to heavy textured soils, particularly for Cd, Co, Cr, Cu, Ni and Zn.

ISO recommend that the ambient background of a substance in soils can be set at a chosen parameter from the frequency distribution of usual concentrations (International Organisation for Standardisation (ISO), 2005). Table 4 shows the range, median, 10th and 90th percentile values for different soil texture groups. The median concentrations of Cd, Co, Cr, Cu, Ni and Zn differ by 3–5 fold between the clayey and sandy texture groups, thus highlighting that soil texture is an important factor affecting trace metal concentrations. In the case of Pb, sandy and peaty soils have the lowest and highest median values, respectively, whereas the other texture groups show similar median values (Table 4). The median values for each soil texture group can be considered to represent the median ambient background concentrations (MABCs) of the group. This approach, although not perfect, represents a significant refinement in the way that it takes into account a key soil property that is easily measurable in a site investigation.

Alternatively, the ABC could be set at the 90th percentile value for each texture group (Table 4) (International Organisation for Standardisation (ISO), 2005). However, such values can be considered as representing the upper limits of the ABC range for each soil texture group. It should be pointed out that, according to the European Technical Guidance Document for risk assessment (European Commission, 2003), the 90th percentile values are taken as the reasonable worst-case predicted environmental concentrations (PEC) (Heijerick et al., 2006). Thus, ABCs set at the median values (i.e. MABCs) would avoid potential confusion with the reasonable worst-case PEC.

3.4. ABC for Pb in soils derived from the probability graph approach

Fig. 4 shows the cumulative frequency distributions for the log-transformed concentrations of Pb. At the low Pb concentrations, the frequency distribution curve generally appeared to be linear, except for a very small proportion of data with the lowest concentrations that tended to lie off the straight line. The linearity of the lower part of curve is consistent with a hypothesis

Table 4
Summary statistics of trace metal concentrations according to soil texture groups

Soil texture group ^a	Minimum	10th percentile	Median	90th percentile
Cd				
Clayey	<0.2	0.6	1.0	1.6
Fine loamy	<0.2	0.4	0.8	1.3
Fine silty	<0.2	0.5	0.9	1.7
Coarse silty	<0.2	0.3	0.7	1.4
Coarse loamy	<0.2	<0.2	0.5	1.0
Sandy	<0.2	<0.2	<0.2	0.6
Peaty	<0.2	<0.2	0.6	1.2
Co				
Clayey	3.9	9.6	14	20
Fine loamy	<0.5	5.8	11	19
Fine silty	0.6	6.3	13	20
Coarse silty	1.3	5.2	10	18
Coarse loamy	<0.5	2.8	7.1	14
Sandy	<0.5	0.6	3.1	7.6
Peaty	0.8	0.7	1.7	9.3
Cr				
Clayey	19	43	59	83
Fine loamy	5	29	44	64
Fine silty	6	29	48	66
Coarse silty	6.3	23	39	66
Coarse loamy	<1	16	27	45
Sandy	<1	5.7	13	27
Peaty	<1	3.5	12	39
Cu				
Clayey	6.9	16	23	39
Fine loamy	3.7	11	19	36
Fine silty	4.0	11	19	32
Coarse silty	5.8	11	19	35
Coarse loamy	1.8	7.0	15	38
Sandy	1.2	3.3	7.4	21
Peaty	1.9	6.4	15	44
Ni				
Clayey	11	25	38	51
Fine loamy	1.6	14	25	41
Fine silty	2.3	15	28	44
Coarse silty	4.5	13	22	39
Coarse loamy	<2	6.8	16	29
Sandy	<2	2	7.5	18
Peaty	<2	2.9	6.6	24
Pb				
Clayey	6	21	35	71
Fine loamy	<4.7	21	39	99
Fine silty	<4.7	24	39	92
Coarse silty	13	20	42	103
Coarse loamy	5	18	36	114
Sandy	<4.7	10	22	55
Peaty	8	35	116	314
Zn				
Clayey	36	75	106	157
Fine loamy	16	54	89	151
Fine silty	19	57	90	156
Coarse silty	18	50	78	145
Coarse loamy	10	33	65	132
Sandy	5	12	35	86
Peaty	12	23	52	104

Concentrations of all elements are in mg kg⁻¹.

^a Number of samples for different texture groups: clayey = 483, fine loamy = 2002, fine silty = 1061, coarse silty = 182, coarse loamy = 1141, sandy = 228, peaty = 557.

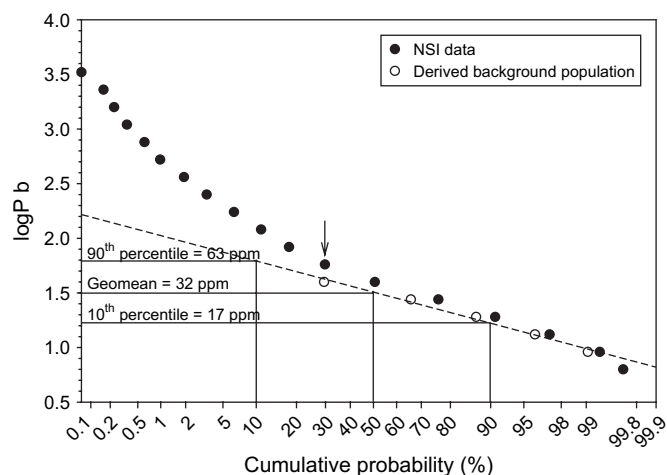


Fig. 4. Probability graph for soil Pb concentration. Arrow indicates the inflexion point.

that the metal concentrations represent uncontaminated soils in which the frequency distribution is lognormal (Davies, 1983). The departure from linearity at the lowest level is likely to be due to the problem of metal concentrations being around or below the detection limit; this small portion of data can be ignored. The next step was to identify the % cumulative frequency at which the straight line changes into a complex curve, i.e. the inflexion point (indicated by an arrow in Fig. 4). The inflexion point for Pb was at 30%, implying that 30% of all soil samples are from “contaminated” soils and 70% from “uncontaminated” soils. A new cumulative frequency distribution for the “uncontaminated” soils (F') was then calculated as $F' = 100 - (100 - F) \times (100/70)$, where F is the cumulative frequency for the original data (Sinclair, 1974). A new line was then plotted of the relationship between $\log_{10}\text{Pb}$ and F' (Fig. 4), which represents the log-normal distribution of the “uncontaminated” population. The mean $\log_{10}\text{Pb}$ value corresponds to 50% cumulative frequency on the new straight line and its antilog is the geometric mean (32 mg kg^{-1} Pb) of the arithmetic data. This value agrees well with the range of $30\text{--}50 \text{ mg kg}^{-1}$ given by Davies (1983) who used much smaller datasets for soils in England and Wales. The 10th and 90th percentile values of this population of “uncontaminated” soils can also be readily determined as 17 and 63 mg kg^{-1} Pb.

However, the probability graph approach has several shortcomings. First, it generates a single mean value and a single percentile range for the whole database, and thus ignores the possibility of ABC varying for different soil types. Second, the assumption that only the population representing the lowest metal concentrations is “uncontaminated” may be too simplistic. When the probability graph method was applied to the data for Cd, Co, Cr, Cu, Ni and Zn, the “uncontaminated” population was overly represented by soils of light textures, suggesting that their relatively low concentrations are partly due to the effect of soil type (data not shown). Only in the case of Pb did the “uncontaminated” population consist of different texture groups in similar proportions to those in the whole dataset, except that peaty soils are

underrepresented, due to the elevated Pb concentrations in many upland peats referred to above. Therefore, use of the probability graph approach may be suitable for deriving a country-wide ABC for Pb, but not for other trace metals in this dataset. For Pb, the ABC obtained by the probability graph method (32 mg kg^{-1}) is similar to the median values of different soil texture groups except peaty and sandy soils (Table 4).

3.5. Potential uses of ABCs

The regulation of metals in soils (and waters) for environmental protection is fraught with a number of significant problems, including issues of essentiality, bioavailability, toxicity and variability in background concentrations. The development and application of practical and robust methods to predict ABCs, and given appropriate databases, will enable the site-specific assessment of soils in a number of regulatory regimes at the national and international level. Examples include assessment of contaminated land (Department of the Environment Transport and the Region, 2000), codes of good agricultural practice (Ministry of Agriculture Fisheries and Food, 1993), pollution prevention and control (European Commission, 1996) and the European Union Soil Thematic Strategy (European Union Soil Thematic Strategy, 2002).

In terms of environmental risk assessment (European Commission, 2003), it is important to note that the data available for metal toxicity assessment for invertebrates, plants and soil microbes uses the ambient background soil concentrations as a ‘control’ to which metal doses are added in the testing procedure (e.g. Oorts et al., 2006b; Rooney et al., 2006). This ambient background soil concentration is often subtracted from the final calculated toxicity statistic to give a value without the inclusion of background metal. Thus, the toxicity “effect concentrations” (e.g. EC_{10} or EC_{50}) are based on the added metals. For site specific risk characterisation, the Predicted No Effect Concentrations (PNECs) which are derived through statistical processes from these data can, for example, be compared to a measured soil concentration at the site of interest (PEC) from which the predicted ABC has been subtracted (denoted PEC_{add}). This subtraction of potentially confounding background concentrations of metal from the measured environmental concentration enables a more appropriate comparison of PEC and PNEC values including the determination of a risk characterisation ratio ($\text{PEC}_{\text{add}}/\text{PNEC}_{\text{add}}$). This refinement is the first step towards correcting the measured exposure concentration at the site to the exposure concentration in the laboratory toxicity tests. A further adjustment, if necessary in a stepwise approach, would be an allowance for the “ageing” effect of metals over time after addition to soils in the field, which is a subject of active research presently (Lock and Janssen, 2003a,b; Oorts et al., 2006a).

Finally, by refining the measured soil concentration at the specific site and using appropriate PNECs, regulators can set single guideline values or standards for metals that would apply nationally.

4. Conclusions

The requirement to perform risk assessment of trace metals in soil is key to many regulatory regimes and environmental protection measures, and this requires prediction of site-specific or soil type-specific ABCs.

Analysis of the geochemical data for soils in England and Wales show a strong association between the trace metals Co, Cr and Ni and the major elements Al and Fe. Multiple regressions linking the log-transformed concentrations of Co, Cr or Ni with Al and Fe were obtained, which explained 62–85% of the variation in the trace metal concentrations. Site-specific ABCs of Co, Cr or Ni in topsoils could be predicted reasonably well from soil Al and Fe concentrations. There was no strong association between the trace metals Cd, Cu, Pb or Zn with Al and Fe, which is consistent with geochemical principles. Therefore, site-specific ABCs of these trace metals could not be predicted reliably using regressions with Al and/or Fe.

Soil texture has a major influence on trace metal concentrations, with heavy textured soils having higher concentrations of Cd, Co, Cr, Cu, Ni and Zn than light soils, and peaty soils having higher Pb concentrations than other soils. Median concentrations of trace metals were calculated for seven soil texture groups, and can be used as soil texture-specific ABCs.

A probability graph approach was used to identify an “uncontaminated” population of soils from the whole dataset. This approach yielded estimates of the geometric mean and the 10th–90th percentile range of trace metals that might be associated with the “uncontaminated” population in the region. However, this method may be appropriate only for Pb, because for other trace metals the “uncontaminated” population was over-represented by soils with light textures.

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