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Baseline concentration levels of trace elements as a function of clay and organic carbon contents in soils in Flanders (Belgium)

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Abstract

Baseline concentration levels of trace elements in the soils of Flanders (Belgium) were assessed as a function of clay and organic carbon contents. Outliers in the data were identified and rejected according to statistical criteria. Median trace element concentrations in mg/kg dry weight were As 7, Cd 0.18, Co 0.05, Cr 24.6, Cu 9.6, Hg 0.17, Ni 3.5, Pb 21.5, Zn 34.5. Clay and organic carbon contents were found significant in predicting soil trace element contents in unpolluted soils. The coefficients of determination ranged from 0.07 (Hg) to 0.69 (Ni). Based on confidence intervals of the observations, trace element concentrations that have a known probability of being exceeded can be assessed as a function of clay and organic carbon content and used as soil quality reference values.

Keywords: Trace elements; Baseline concentrations; Belgium

1. Introduction

Free of human interference, the trace element contents of soils depend largely on the mineralogical composition of the parent material and on the processes of weathering to which the soil forming materials have been subjected [1]. Besides, trace elements originating from various sources may reach the surface soil, and their further fate depends on soil chemical and physical properties[1–3]. Trace element concentrations in topsoils are likely to increase with growing industrial and agricultural activities. Due to the long distance aerial transport of trace pollutants, it has become difficult to estimate the true geochemical background levels of trace elements in soils. Geochemical background concentrations should represent natural concentrations, which ideally exclude human influence. Geochemical baselines, in contrast, represent a concentration specific to one area and time and are not always true backgrounds [2,4].

For legislation purposes, soil quality reference values are being developed in different countries. In this context, there is a need to establish levels of trace elements currently found in common soils. Reference values for clean soil may be based on baseline concentration levels currently found in soils that are considered clean, and may differ between countries and/or geographical regions.

The extent by which trace elements are retained by soils is strongly related to soil properties. Soils containing high amounts of clay minerals and organic matter will tend to accumulate higher metal levels because these compounds have pronounced metal binding properties [5]. The purpose of this study was to assess baseline concentration levels of trace elements currently found in soils of the Flemish region as a function of clay and organic carbon contents. Surface soils in Flanders were sampled from 0–20 cm and soil characteristics and total element contents were assessed. Samples were taken from arable land, forest, fallow land and pasture, and the resulting data set was analysed to assess current concentration levels of trace elements in Flemish soils that are not subjected to particular point sources of contamination.

2. Experimental

2.1. Compilation of the data

Data on soil characteristics and total trace element contents of soils in the Flemish region (Belgium) were compiled from various sources. Most data originated from a survey on soil and plant element contents, conducted by the laboratory of Applied Analytical Chemistry and Ecochemistry in 1979 and 1980. Up to 494 points were sampled in an area covering approximately 630 km^2 between the cities of Ghent and Antwerp [6]. Data on 25 samples from all over Flanders were made available by the Flemish Institute for Technological Research (VITO) [7]. Finally, 24 additional samples with loam and clay texture were taken and analysed in the summer of 1995.

Soils in Flanders are mostly derived from recent sedimentary parent materials deposited during the Pleistocene or Holocene. Geographical regions in Flanders (Fig. 1), often named according to the dominant soil texture, are represented by one or two major soil types.

- The *coastal dune belt* consists of recent eolian sandy deposits and is characterised by dry calcareous soils without significant profile development.

The *polder* area consists of Holocene marine, mostly clayey deposits overlying a sandy or peaty subsoil.

- In the *sandy area* most soils are developed of eolian sands of Pleistocene age. Podzols, i.e. strongly leached acid soils, are very common.
- Soils in the *sandy loam area* and *loam areas* are developed on eolian materials of Pleistocene age. The sandy loam was deposited nearer to the source area (North Sea basin) than the loess, which has been transported further south due to its finer texture. The representative soils show a clay illuviated subsurface horizon (Bt horizon).

Sampling locations were selected in agricultural land (85% of all samples), forest (7%), pasture (5%) or fallow land (3%) and are indicated in Fig. 1. On each sampling location, a composite of at least four subsamples of soil was collected within a 20-m radius of the selected sampling point. Soils were sampled from a depth of 0-20 cm using a hand borer and stored in polyethylene bags. Soils were air-dried and ground to pass a 2-mm sieve.

Organic carbon was determined by the Walkley and Black method [8]. The pH of the soils was measured in a suspension of 10 g soil in 50 ml H_2O after 24 hours [9]. Total trace element contents were determined as aqua regia extractable amounts [10]. Metals in the extracts were measured with flame (air/acetylene gas) atomic absorption (Varian SpectrAA-10) using external standards, prepared in 2% nitric acid from 1000 mg/litre stock solutions of the metals (Merck). Mercury was determined by cold vapour atomic absorption (Coleman Mercury Analyser, Mas-50) after a specific destruction [9]. Quality control was assured by the use of duplicates, standard reference materials (estuarine sediment CRM 277 and light sandy soil CRM 142 R) and procedural blanks. Standard deviations on a triplicate analysis of a soil sample in our laboratory were: 0.7 mg/kg for Cd at 9.2 mg/kg, 9 mg/kg for Cu at 100 mg/kg, 1 mg/kg for Co at 11 mg/kg, 3 mg/kg for Ni at 40 mg/kg, 12 mg/kg for Pb at 140 mg/kg, and 75 mg/kg for Zn at 538 mg/kg.

Soil clay contents were determined using the pipette method [11]. Clay contents for the soils from the survey were estimated from clay contents in neighbouring similar soils. These data were obtained from the database "AARDEWERK" that contains data about 13033 profiles in Belgium [12].Using the geographic information system ARC-Info, clay contents at the sampling points were estimated as the distant weighed average of values from data points that were (1) situated within a radius of 5 km (2) within the same textural class according to the Belgian texture triangle [13] and (3) with the same soil use (forest, agricultural land or pasture).

2.2. *Data processing*

To estimate current baseline concentration levels, multiple linear regression was performed using clay and organic carbon content as predictor variables. Statistical confidence limits are reliable only if the assumptions of the statistical method are met [14]. To achieve approximate normality and equality of variance of the residuals, the independent and dependent variables were log-transformed (As, Cr, Cu, Hg) or square-root-transformed (Cd, Co, Ni, Pb, Zn) [15].

Before constructing the final models, the data were screened to reject apparently contaminated soils, i.e., soils with high, outlying total contents. For that purpose, multiple regression was performed using all data. Cases for which the observed value was higher than the estimated value + 2 times the standard deviation of the residuals were considered outliers and excluded. Although some soils with particularly high total contents are easily discerned on a plot (e.g. Fig. 2), other outlying values may be more difficult to identify. The use of statistical criteria allowed a more objective screening of the data.

The regression was then recalculated using the selected data to yield estimated values and 90% confidence limits of the observation for current baseline concentration levels in normal Flemish soils as a function of clay and organic carbon content. Only independent variables that were significant at the 5% level were retained in the final model. Transformation of the data improved the normality of the residuals, although generally a distinctive negative kurtosis remained. The example of Zn is shown in Fig. 3. Variances became quite homogeneous over the entire range of the independent variables as a result of the transformation (Fig. 4). The assumptions of the linear regression were therefore only partially fulfilled. This implies that calculated confidence intervals are not exact. However, they may be sufficiently accurate for practical purposes. The most suitable transformation of the data (square root or log transformation) was selected after visual inspection of plots for the different elements similar to these in Fig. 3 and 4.

3. Results and discussion

3.1. *Trace element contents*

Sampling points with outlying element contents were identified and rejected according to statistical criteria (See *Experimental*). Table 1 summarises statistics for the retained sampling points. All elements, except Hg, were within the range reported for soils of central eastern Europe [4] and within ranges reported from various sources by Adriano [1]. This suggests that trace element contents in common Flemish soils are not largely affected by human activities.

In contrast, the range for Hg was larger than these reported for normal soils. Mercury is present naturally in soils at concentrations ranging from a few µg/kg to a few hundred µg/kg [1]. While mean and median values were in the order of 100 µg/kg, values up to 2.26 mg/kg were considered to be representative for current Hg concentrations in common Flemish soils. This would suggest a widespread significant impact of human activities on Hg-concentrations in Flemish soils.

Relatively few soils were denoted ‘contaminated’ and excluded before determining baseline concentration levels (Table 2). These soils have a significantly higher total content compared to the bulk of the data. For several of these soils, contamination was related to historical land disposal of contaminated dredged materials from the river Schelde in the neighbourhood of Antwerpen [6].

3.2. *Baseline concentration levels as a function of clay and organic carbon content*

The fitting statistics for the models that describe the total contents as a function of clay and organic carbon contents are given in Table 3. R^2-values were rather low, indicating that the predictor variables only partially explain the total variance. Other factors as soil genesis and clay mineralogy also determine the total element contents in soils [1,2]. Input of trace elements in soils is expected to occur in a random way. Both diffuse atmospheric deposition rates and input through fertiliser use are highly variable in time and in space [2].

Except for Cr and Hg, both clay and organic carbon contents were significant in predicting total trace element contents. Because of their binding properties for trace elements, these constituents will enhance the accumulation of trace elements in the soil. Organic carbon content was not significant in predicting Cr and Hg-contents when clay content was already introduced in the regression model. For Cr, R^2 was high (0.562) despite the fact that only clay was a significant predictor variable. Clay content explained only 7.3% of the total variability in Hg-contents. Mercury concentrations were significantly affected by human impact, which is a random factor in time and space. While clay and organic carbon contents may be major factors determining the retention of trace elements that mainly occur in cationic forms (e.g. Zn, Cu, Pb), the more complex environmental chemistry of Hg implies that several mechanisms may significantly control Hg retention. For example, the retention of Hg in soil is not only caused by valence-type ionic adsorption by organic and inorganic materials. It may also be retained by formation of covalent bounds with organic compounds or by precipitation as highly insoluble carbonates, phosphates or sulphides [1,3].

The regression equations allow to predict the expected contents of an element from the clay and organic carbon contents of the sample. In Figs. 5 to 7, the expected contents and the upper 90% confidence interval of the observation are plotted for organic carbon levels of 1 and 3 %. For approximately 90% of our observations, the organic carbon content was within that range. Because the observed range in organic carbon content in Flemish soils is more narrow than the range in clay content, clay content is generally the most relevant factor in predicting soil element contents.

In Table 4, expected total contents and upper 90% confidence limits of the observation are presented for varying clay and organic carbon contents. If a soil is ‘normal’ or ‘unpolluted’, the probability to find a total content higher than this upper confidence limit is only 5 percent. Such confidence limits of the observation may be used as reference values to determine whether a soil is contaminated. This indication of contamination only implies that the total contents are higher than normally can be expected in unpolluted areas. No indications may be inferred about potential risk for environmental hazards that may exist as a result of the observed element contents.

4. Conclusions

A multiple regression approach allowed to assess baseline concentration levels of trace element in Flanders as a function of clay and organic carbon contents. Results indicated that, with the exception of Hg, baseline concentrations in common soils in Flanders are not significantly affected by human impact. Trace element levels that have a known probability of being exceeded can be assessed and used as soil quality reference values.

Although the presented procedure constitutes a valuable first approach in evaluating the extent of soil pollution, it is in no way an effect oriented quality assessment. Not only the presence, but also the physico-chemical and biological behaviour of the pollution should be assessed. In this respect, standard values for the total concentration of trace elements in soils should be assigned an alerting function only. When trace element contents at a given site are comparable to current baseline concentration levels, it may be assumed that the situation is normal and that no ‘hazardous effects’ are expected to occur.

5. Acknowledgement

We wish to thank the “Openbare Afvalstoffenmaatschappij voor het Vlaamse Gewest” (OVAM) for their support in this research.

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Table 1.
Metal contents and ranges in soils retained for the determination of baseline concentration levels

	Mean	Median	Range	*N*
As	10.5	7.0	0.82–95	162
Cd	0.33	0.18	0.02–5.3	456
Co	0.42	0.05	0.03–7.7	408
Cr	25.7	24.6	1.17–119	147
Cu	10.6	9.6	1.7–39	463
Hg	0.30	0.17	0.01–2.26	153
Ni	4.1	3.5	0.3–23	457
Pb	24.4	21.5	0.0–132	454
Zn	39.7	34.5	6.1–208	461

Table 2.
Metal contents and ranges in rejected soils

	Mean	Median	Range	*N*
As	69.8	68.0	18.1–160	7
Cd	5.7	6.13	1.9–13.8	15
Co	4.86	4.41	0.45–11.5	14
Cr	322	317	34–615	3
Cu	60.8	49.3	10.9–133	8
Hg	2.49	2.92	1.49–3.07	3
Ni	15.9	12.7	11.4–38.7	14
Pb	131	102	38.9–244	17
Zn	638	370	129–1816	10

Table 3
Fitting statistics for the various elements

Element	Transformation[a]	Significant variables[b]	*N*	R^2
As	LOG10	Clay, OC	162	0.540
Cd	SQRT	Clay, OC	456	0.417
Co	SQRT	Clay, OC	408	0.619
Cr	LOG10	Clay	147	0.562
Cu	LOG10	Clay, OC	463	0.247
Hg	LOG10	Clay	155	0.073
Ni	SQRT	Clay, OC	445	0.691
Pb	SQRT	Clay, OC	454	0.240
Zn	SQRT	Clay, OC	461	0.373

[a] Logarithmic (LOG10) or square root (SQRT) transformation of the dependent and independent variables

[b] Organic carbon (OC) was excluded from the model when the significance level was lower than 5%

Table 4
Expected total contents and upper 90% confidence limits of the observation in mg/kg dry soil as a function of clay and organic carbon contents

	Expected total content					
Clay (%)	5		15		25	
OC (%)	1	3	1	3	1	3
As	5	8	9	13	11	17
Cd	0.1	0.3	0.4	0.7	0.7	1.0
Co	0.1	0.4	0.6	1.1	1.2	1.8
Cr	18	18	30	30	38	38
Cu	9	11	11	14	12	15
Hg	0.1	0.1	0.2	0.2	0.2	0.2
Ni	3	4	5	7	7	9
Pb	18	27	24	35	29	40
Zn	32	43	45	57	54	68

	90% upper confidence limit of the observation					
Clay (%)	5		15		25	
OC (%)	1	3	1	3	1	3
As	12	18	20	31	26	40
Cd	0.6	1.0	1.1	1.5	1.5	2.0
Co	0.6	1.1	1.5	2.2	2.3	3.2
Cr	37	37	61	61	77	77
Cu	17	21	21	26	23	29
Hg	1.1	1.1	1.6	1.6	1.9	1.9
Ni	6	8	10	12	13	15
Pb	38	51	47	60	53	68
Zn	56	70	72	88	84	101

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Fig. 7. Observed data, expected trace element contents and upper 90% confidence limits of the observation as a function of clay content for organic carbon levels of 1% and 3% for Ni, Pb and Zn.

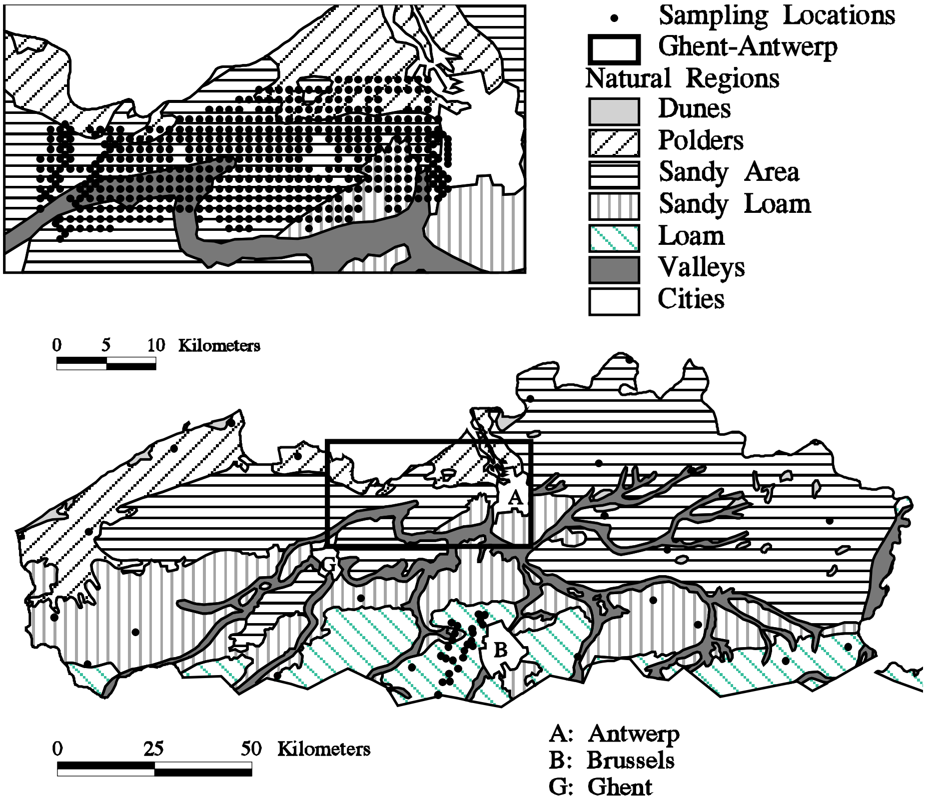
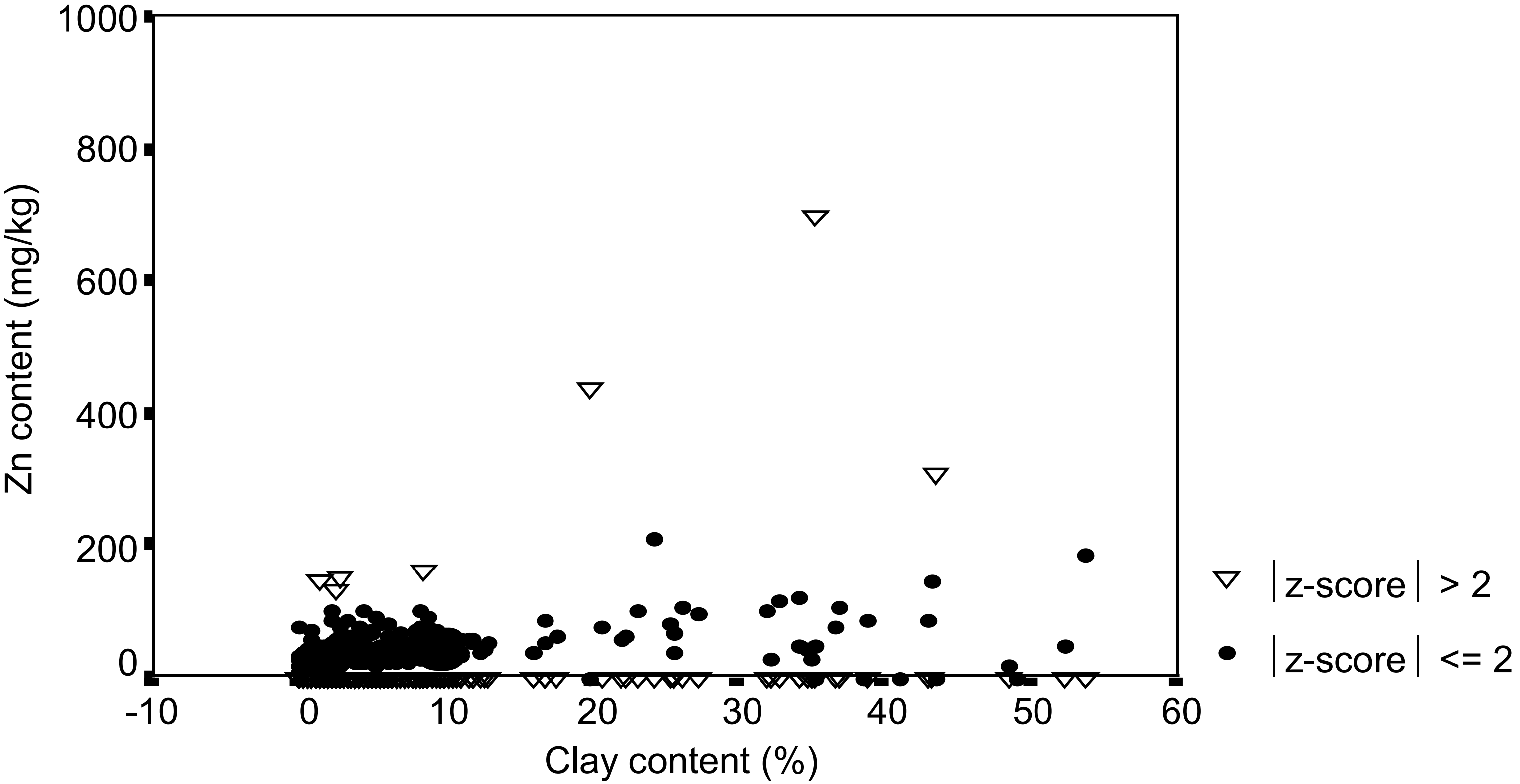

Sampling Locations
Ghent-Antwerp
Natural Regions
Dunes
Polders
Sandy Area
Sandy Loam
Loam
Valleys
Cities
0 5 10 Kilometers
A
B
G
0 25 50 Kilometers
A: Antwerp
B: Brussels
G: Ghent

Fig. 1



1000
800
600
400
200
0
-10
0
10
20
30
40
50
60
Zn content (mg/kg)
Clay content (%)
▽ │z-score│ > 2
● │z-score│ <= 2

Fig. 2

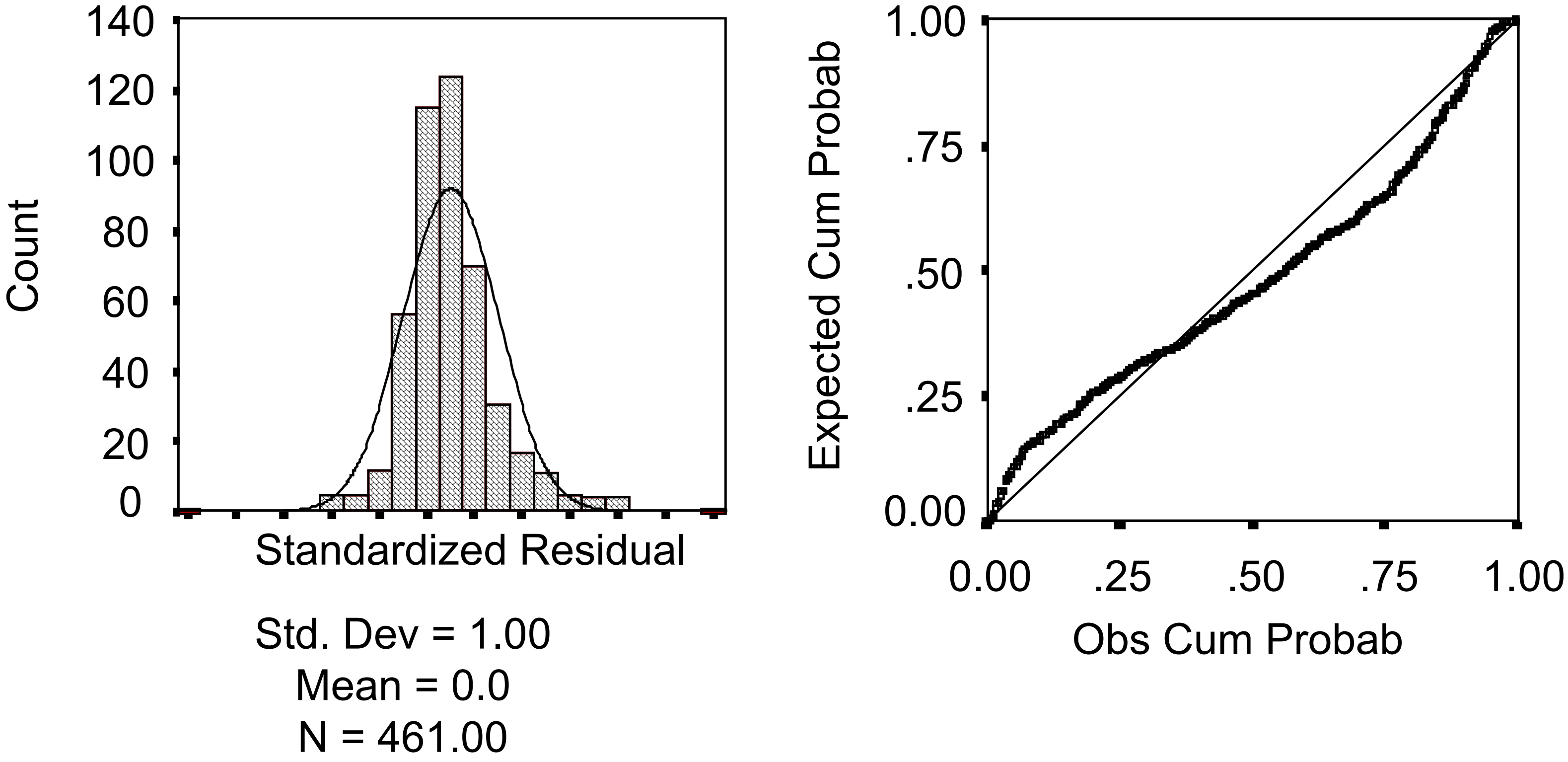


Fig. 3

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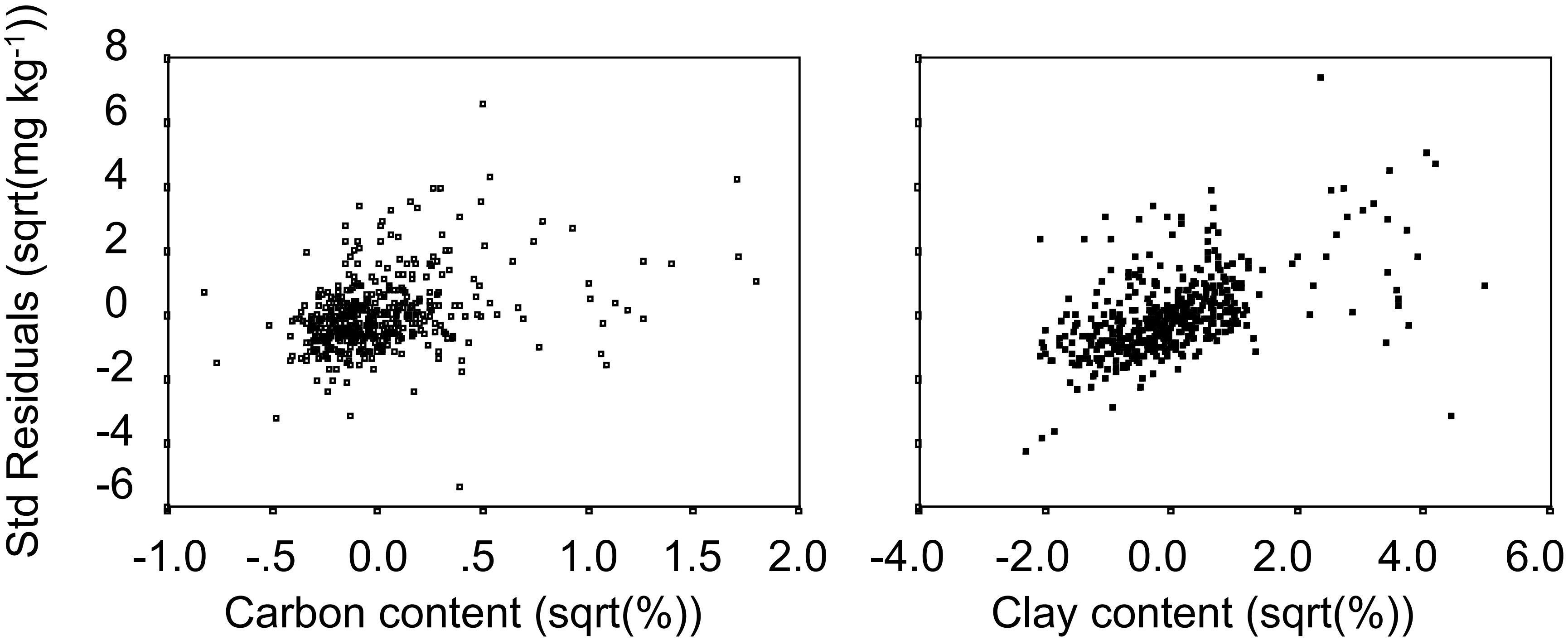

Fig. 4

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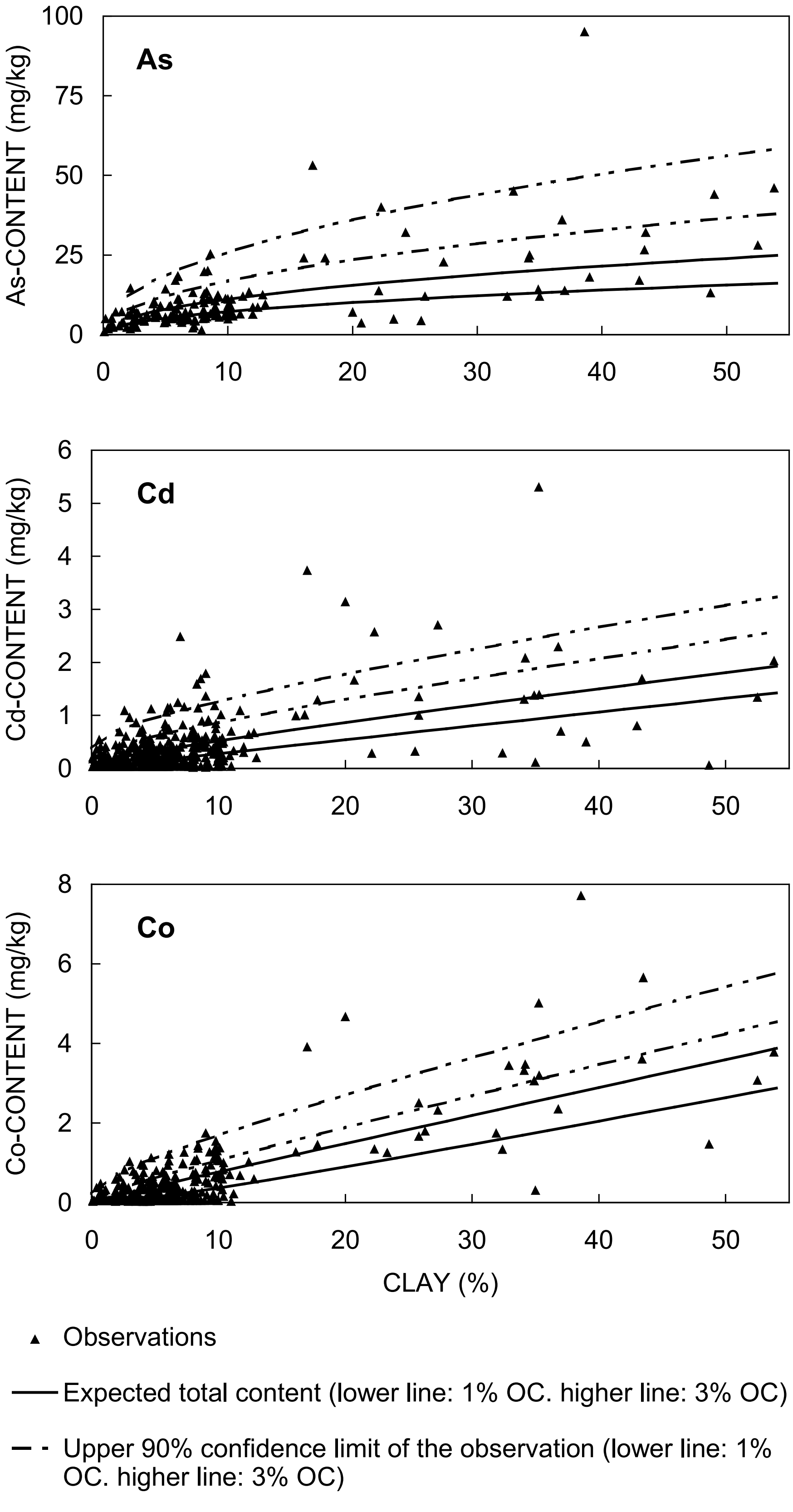
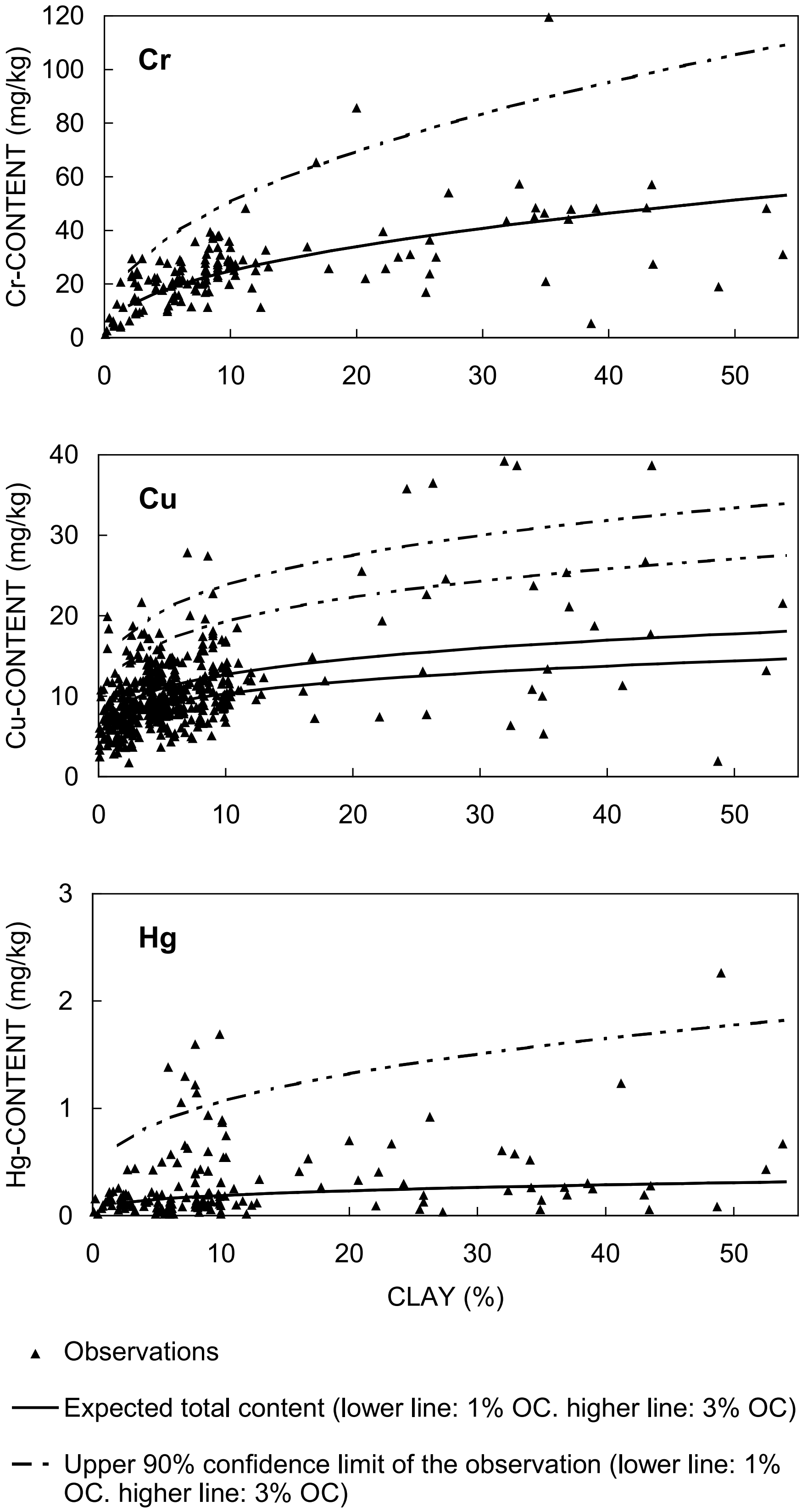

As
As-CONTENT (mg/kg)
0
25
50
75
100
0
10
20
30
40
50
Cd
Cd-CONTENT (mg/kg)
0
1
2
3
4
5
6
0
10
20
30
40
50
Co
Co-CONTENT (mg/kg)
0
2
4
6
8
0
10
20
30
40
50
CLAY (%)
▲ Observations
Expected total content (lower line: 1% OC. higher line: 3% OC)
Upper 90% confidence limit of the observation (lower line: 1% OC. higher line: 3% OC)

Fig. 5


Cr
Cr-CONTENT (mg/kg)
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20
40
60
80
100
120
0
10
20
30
40
50
Cu
Cu-CONTENT (mg/kg)
0
10
20
30
40
0
10
20
30
40
50
Hg
Hg-CONTENT (mg/kg)
0
1
2
3
0
10
20
30
40
50
CLAY (%)
▲ Observations
Expected total content (lower line: 1% OC. higher line: 3% OC)
Upper 90% confidence limit of the observation (lower line: 1% OC. higher line: 3% OC)

Fig. 6

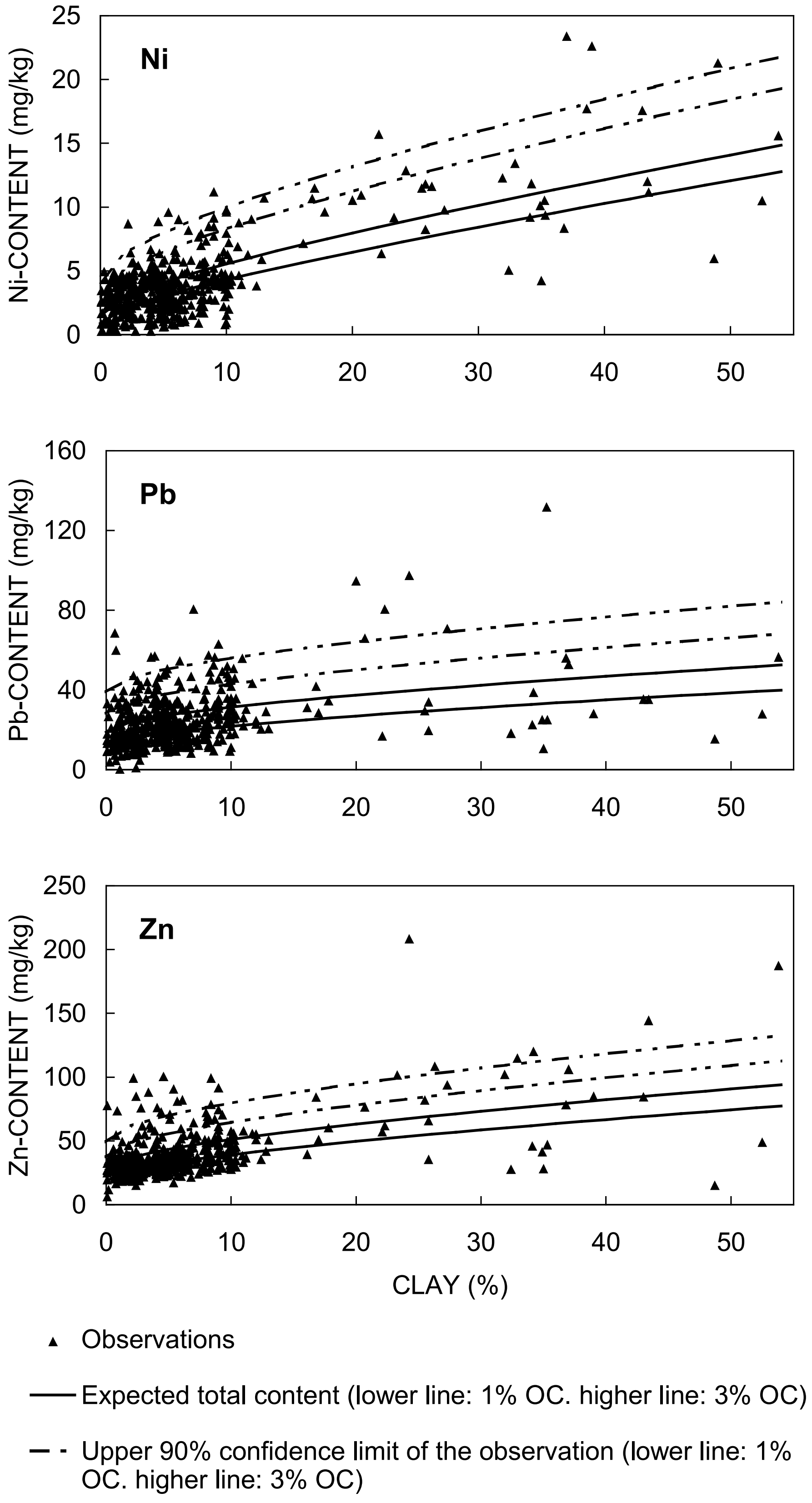
Ni
Ni-CONTENT (mg/kg)
0
5
10
15
20
25
0
10
20
30
40
50
Pb
Pb-CONTENT (mg/kg)
0
40
80
120
160
0
10
20
30
40
50
Zn
Zn-CONTENT (mg/kg)
0
50
100
150
200
250
0
10
20
30
40
50
CLAY (%)
▲ Observations
Expected total content (lower line: 1% OC. higher line: 3% OC)
Upper 90% confidence limit of the observation (lower line: 1% OC. higher line: 3% OC)

Fig. 7