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Modelling trace metal background to evaluate anthropogenic contamination in arable soils of south-western France

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A B S T R A C T

The trace metal (TM) content in arable soils has been monitored across a region of France characterised by a large proportion of calcareous soils. Within this particular geological context, the objectives were to first determine the natural levels of trace metals in the soils and secondly, to assess which sites were significantly contaminated. Because no universal contamination assessment method is currently available, four different methods were applied and compared in order to facilitate the best diagnosis of contamination. First, the TM geochemical background was determined by using basic descriptive statistics and linear regression models calculated with semi-conservative major elements as predictors. The natural concentrations of trace metals varied greatly due to the high soil heterogeneity encountered on the regional scale and were more-or-less accurately modelled according to the considered TM. Second, the basic descriptive statistics and the linear regression methods were then compared with the enrichment factor (EF) method and multivariate analysis (PCA), in order to evaluate whether the concentrations measured in soils were abnormally high or not. The advantages and disadvantages of each method were discussed and their results used to identify the most probable contamination cases, the influence of the soils characteristics, as well as the agricultural land cover. The basic descriptive method was good as a first and easy approach to describe the TM ambient concentrations, but may misinterpret the natural anomalies as contaminations. Based on geochemical associations, the linear regression method provided more realistic results even if the relationships between major and trace metals were not significant for the most mobile TM. The EF method was useful to identify high point source contaminations, but it was not suitable when considering a large dataset of low TM concentrations. Finally, the PCA method was a good preliminary tool for the description of the global TM concentrations in a studied area, but it could only give indication on the highest contaminated points. By comparing the results of the different methods in the studied region, we estimated that 24% of the arable soils were contaminated by at least one trace metal, mainly Cu in vineyards/orchards and Cd, Pb and/or Zn in grazing lands. In addition, the calcareous soils exhibited globally higher natural and anthropogenic TM concentrations than non-calcareous soils, probably because of the lower TM mobility at alkaline pH.

Keywords:

Trace metals
Agricultural soil
Model
Statistics
Calcareous
Agricultural land cover

1. Introduction

Soils constitute a limited and non-renewable resource that needs to be protected; however, they are subject to contamination by various trace metals (TMs). Atmospheric deposits from smelter-related industries or gas combustion, use of chemicals to prevent crop disease, irrigation and application of NPK fertilisers, manures and sewage sludge are multiple sources that contribute to the elevation of TM levels in arable soils (Het et al., 2005). Therefore, monitoring the TM concentrations in arable soils is necessary for the protection of soil quality and food safety. A sustainable

management of soils requires the determination of the TM geological background in order to evaluate the quantities of TMs originating from anthropogenic and natural sources (Baize and Sterckeman, 2001). On the one hand, the anthropogenic fraction is the result of low to moderate diffuse inputs into the soil and of point sources of contamination. On the other hand, the natural background is variable depending on the soil type, because both the parent material and the pedogenesis influence the natural metal concentrations (Bini et al., 2011; Wilson et al., 2008). Consequently, the range of local background concentrations must be defined on a regional scale in order to quantify accurately the fraction of exogenous metals.

Soil quality guidelines are available in several countries of the world as indicative levels for the protection of environmental and human health. However, European countries are still in discussion to

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establish common soil protection policies. Usually, different national guidelines are used as limits to define the utilisation potential of arable soils, but these concentration levels are usually high and do not reflect the natural local concentrations. Several soil monitoring programmes have been carried out on a national scale to measure the ranges of TM concentrations usually encountered in soils. Such concentration ranges might be good indicators of the natural background but they do not truly evaluate the natural variations on a regional scale.

In the Midi-Pyrénées region of south-western France, a large proportion of soils were formed on typical calcareous bedrocks. Most studies in calcareous soils have shown a high retention of heavy metals on carbonates after application of the contaminants in soil columns (Lafuente et al., 2008; Ouhadi et al., 2010; Plassard et al., 2000) but the behaviour of natural TMs in these soils remains rarely studied because carbonate rocks are not very common across the globe (Amiotte-Suchet et al., 2003). Within this particular geological context, the TM levels in the soils of the Midi-Pyrénées region needs to be better characterised because this region is also one of the largest agricultural areas in France.

Several approaches have been documented in the literature for determining the background TM levels in soils and sediments (Matschullat et al., 2000; Tobias et al., 1997). As the anthropogenic emissions can be transported over long distances and reach apparently undisturbed areas (Hernandez et al., 2003; Steinnes et al., 1997), the background concentrations must be derived from statistical analyses applied to a dataset "clean" of outliers. Probability plots (Fleischhauer and Korte, 1990; Tobias et al., 1997), basic statistics providing 'baseline values' (Mrvić et al., 2011; Reimann et al., 2005; Roca et al., 2008), linear relationships between TMs and elements constitutive of the soil (Hamon et al., 2004; Sterckeman et al., 2006b; Zhao et al., 2007) and sediments (N'guessan et al., 2009; Roussiez et al., 2005; Vijver et al., 2008) and geostatistical predictions (Saby et al., 2009, 2011) are all various methods for estimating the natural levels of TMs in a studied soil dataset.

A second consideration of soil monitoring is the evaluation of anthropogenic contamination. The observed concentrations in investigated soil samples can be compared with decision limits, such as the 'upper-whisker value' of a dataset (Micó et al., 2007) or the theoretical background concentration calculated by linear regression or by geostatistics (Guillén et al., 2011), in order to detect anomalous concentrations. The enrichment factor (Chester and Stoner, 1973) can also be used to determine whether the surface layers of soils or sediments are enriched in TMs compared with an uncontaminated reference material (N'guessan et al., 2009; Reimann and de Caritat, 2005). Moreover, multivariate analyses (principal component analysis (PCA) and cluster analysis) are also useful tools for identifying groups of samples exhibiting concentrations remarkably different to those of the considered soil population (Candeias et al., 2010).

The present study focused on a large collection of arable soils under various agricultural practices in the Midi-Pyrénées region (SW France) to: (1) define the background levels of TMs in two groups of agricultural soils (calcareous and non-calcareous); (2) evaluate the sites contaminated by TMs in relation to the agricultural practices. For this purpose, the approach combined in an original way the use of several methods: statistical description, multiple linear regression, enrichment factor and principal component analysis.

2. Materials and methods

2.1. Geological and soil context of the studied area

The studied region (Midi-Pyrénées) is located in south-western France where various geological and pedogenetic processes occurred. The northern part was formed on volcanic and acidic rocks from the Massif Central in juxtaposition with calcareous and sedimentary rocks. In the central part of the basin, the soils were formed on tertiary

molasse and limestone (for details see Perrin et al., 2008). The south of the region is characterised by the Pyrénées Mountains with calcareous massifs, colluviums, glacial drifts and schist in the piedmont and with sedimentary and metamorphic rocks in the higher mountains. Several valleys with alluvial deposits formed by the main rivers (The Garonne River and its tributaries) also cross the region.

Consequently, both acidic and alkaline soils are well represented across the region. Calcareous soils, such as: Calcosols, Calcisols, Colluviosols, Rendosols and Fluviosols (WRB equivalent: Calcaric and Hypereutric Cambisols, Colluvic Regosols, Renzic Leptosols and Fluvisols) are developed on the molasse calcareous bedrock or on colluvium and alluvium. Non-calcareous soils, such as: Brunisols, Luvisols, Rankosols, Fersialsols and Alocrisols (WRB equivalent: Cambisols, Haplic Luvisols, Umbric Leptosols, Haplic and Hyperdystric Cambisols) originated from acidic bedrocks like gneiss, schist, sandstone, granite, colluvium or alluvium.

The region is mainly cultivated and the dominant land use concerns grasslands, crops, vineyards and orchards. The studied soils have low organic carbon content because forest soils were not considered in the study.

2.2. Sampling and analyses

Two soil collections from agricultural sites were used in this study. On the one hand, 202 composite samples from 123 sites (one or two depths per site) and on the other hand, 57 samples from the deep layer of 57 soil profiles randomly chosen among the 123 sites were collected and analysed (Figure 1). All these samples were collected within the framework of the French soil quality monitoring network (RMQS). The RMQS network is intended for long-term observation of soil properties and chemical characteristics on a 16-km regular grid across the 550,000 km² of French metropolitan territory. The selected sites were at the centre of each 16 × 16 km cell. At each site, 25 core samples per depth were taken following an unaligned sampling design within a 20 × 20 m area and bulked to form one or two composite soil samples per site (0–30 cm surface layer and 30–50 cm layer, if any). For a mechanistic approach, soil profiles were sampled at 57 sites belonging to the 123 sites mentioned above. In each profile, all the soil layers were sampled individually using a core. The number of samples per site ranged from 2 to 7 layers, depending on the thickness of the soil (from 25 to 170 cm deep). The soils were described and classified according to the French soil classification (Baize and Girard, 2009). The bedrock material was also identified at each site. After field sampling, soil samples were air-dried and sieved to pass through a 2 mm mesh before analysis.

The samples were analysed after complete dissolution using a mixture of HNO₃–HF–H₂O₂ following a procedure described in detail in previous studies (Hernandez et al., 2003; N'guessan et al., 2009). Trace elements (Cd, Co, Cr, Cu, Mo, Ni, Pb, Tl, Zn, Cs, Sc and Sn), major elements (Al, Ca, Fe, K, Mg, Mn and Na), and some soil parameters (texture, pH, organic C, and carbonates) were measured at the Soil Analysis Laboratory of INRA at Arras, France (<http://www.lille.inra.fr/las>). Additional elements (As, Sb, Se and V) were also analysed in the profile samples. The concentrations were analysed using an ICP-OES (Thermo IRIS INTREPID II XDL) for the major elements and an ICP-MS (Perkin-Elmer ELAN 6000) for the trace elements (for analytical details see N'guessan et al., 2009).

2.3. Estimation of natural background concentrations

The dataset was divided into two groups of soils following the criteria described in Fig. 2. The CaCO₃ content, the pH, the bedrock and soil types were used to classify the soils between calcareous and non-calcareous soils. For each group, the background concentrations of TMs were estimated by basic statistics and by using multiple linear regressions.

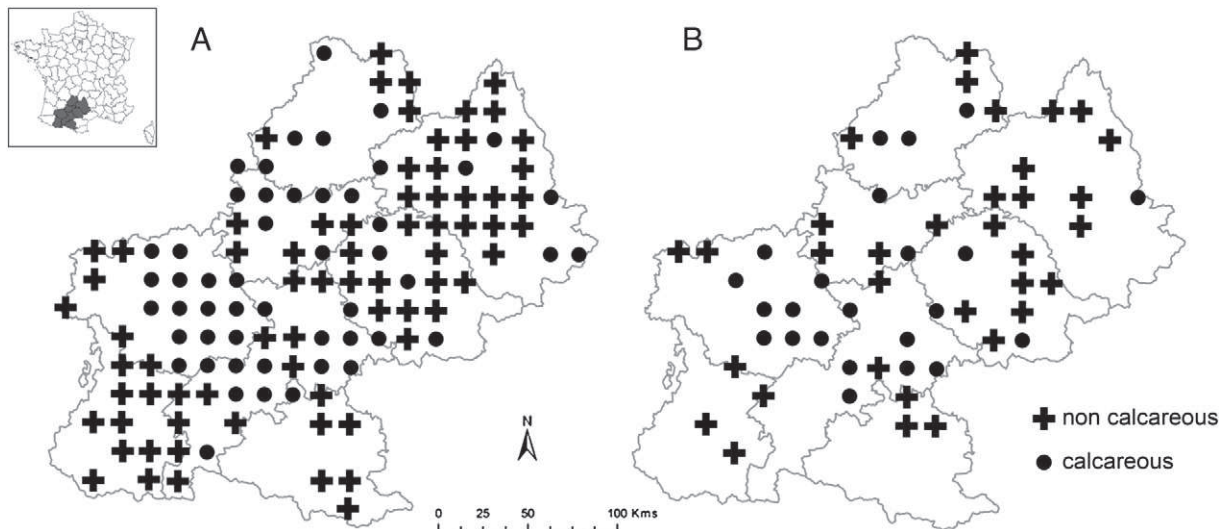


Fig. 1. Maps of the sites sampled for the composite collection (A) and for the profile collection (B) in Midi-Pyrénées (SW France).

2.3.1. Baseline values

Descriptive statistical parameters (number of samples, median, standard deviation, and maximum and interquartile range (IQR)) were calculated for both groups of composite soil samples (one or two layer per site). After removal of the outliers (values > upper-whisker), the mean concentrations and the standard deviation (sd) were calculated to establish the TM baseline levels in calcareous and non-calcareous soils, following the mean + 2 × sd method (Gil et al., 2004; Micó et al., 2007).

2.3.2. Multiple linear regression

The natural background concentrations of TMs were modelled in the deeper layer of the 57 studied profiles, where the metal contents were supposed to be poorly affected by anthropogenic contaminations compared with surface soils. As TMs are naturally present in the primary and secondary minerals (e.g., silicates and oxides) of the soils (Wilson et al., 2008), the background concentrations are supposed to derive from the weathering of these minerals. Therefore,

significant relationships can be found with other elements constitutive of minerals, such as Fe, Al and Mn, which are used as predictors of the natural concentrations of TMs (Anderson and Kravitz, 2010).

Multiple linear regression analyses were applied after In-transformation of the data and after removing the outliers (anomalous concentrations with studentised residuals > 2), in order to model the background concentrations of the TMs in the deep layer of the soil profiles. The best predictors among the concentrations of major elements (Fe, Al, Mn, Mg or Na) were selected following the Mallows's Cp method. Assuming that the relationships between the trace and major elements remain constant along the whole soil profile, the selected linear models were used to calculate the theoretical background concentrations of each TM in the composite soil samples.

2.4. Identification of contaminated samples

Four methods of data analysis were then applied in order to detect the presence of metal contaminations across the studied region. Basic

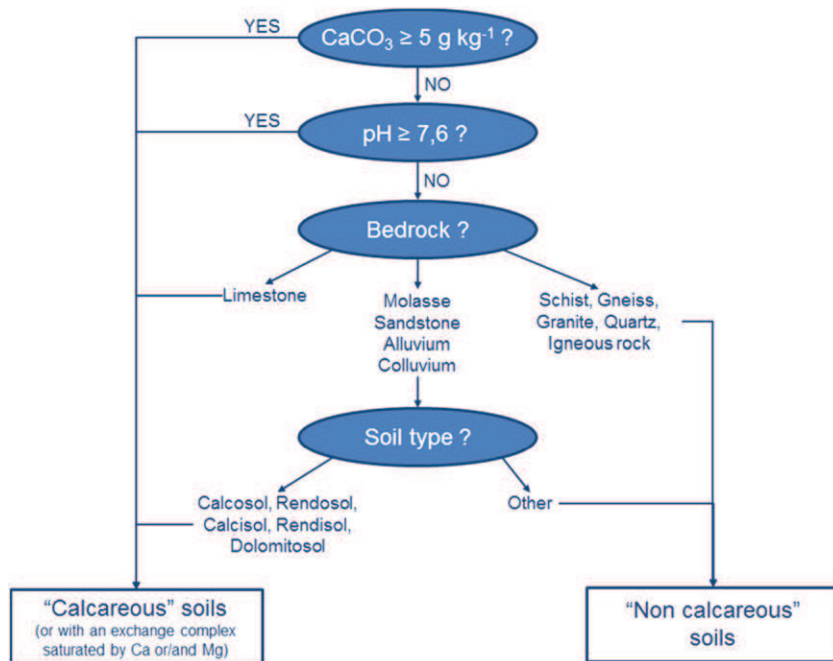


Fig. 2. Scheme of classification between the calcareous and non-calcareous soils of the studied dataset.

Table 1

Median values of the trace metal/Al ratios in the deepest horizons of calcareous and non-calcareous soils of the Midi-Pyrénées region. Trace metal concentrations are in mg kg⁻¹, Al concentration is in g/100 g.

	Cd/Al	Co/Al	Cr/Al	Cu/Al	Mo/Al	Ni/Al	Pb/Al	Sn/Tl	Tl/Al	Zn/Al
Calcareous	0.029*	1.612	9.556*	2.689	0.091	4.780*	3.286	0.522	0.095	14.05*
Non-calcareous	0.014	1.378	7.718	2.305	0.110	3.531	3.402	0.550	0.089	11.43

* Significant difference between calcareous and non-calcareous soil after the Kruskal–Wallis test ($p < 0.05$).

statistics, linear regression analysis, enrichment factor calculation and principal component analysis were performed using the R free software. The Kruskal–Wallis test was used for mean comparison tests.

2.4.1. Upper-whisker value

The upper-whisker value (= 3rd quartile + 1.5 × IQR) calculated from the basic statistics of the composite soil data was used as a limit to define the contamination. Concentrations observed above this limit can indeed be considered as abnormally high compared with the whole dataset. Upper-whisker values were defined in calcareous and non-calcareous soils for each studied trace metal.

2.4.2. Observed vs. theoretical values

The TM concentrations measured in a soil sample should be within the 95% prediction interval of the theoretical concentrations predicted by multiple linear regression based on the major elements contents. Therefore, concentrations in the composite samples above the prediction interval were considered as contamination by exogenous sources.

2.4.3. Enrichment factor (EF)

The enrichment factor (Chester and Stoner, 1973; Hernandez et al., 2003; N'guessan et al., 2009) was used to evaluate the anthropogenic contribution to the TM content in the composite soil collection. The EF was defined as the concentration ratio of a considered trace element (X) to a reference element (Y) in a given sample, divided by the same ratio in a reference material (Eq. (1)). The chosen reference element (Y) was Al because it is a semi-conservative element that has been used in previous studies (Panichayapichet et al., 2007; Reimann and de Caritat, 2005; Sterckeman et al., 2006a; Yay et al., 2008). The total Al concentration was fairly well correlated to most of the trace metals (except Cd) and this data was available for all the studied sites. The deepest layer of the soil profiles was used as the reference

material to take into account the local parent material composition (Hernandez et al., 2003; Sterckeman et al., 2006b). We calculated the X/Y ratio in the deepest layer of the 57 soil profiles and the median (X/Y)_{Reference material} ratios found in calcareous and non-calcareous soils (Table 1) were used in the EF calculation.

$$EF = \frac{(X/Y)_{\text{Sample}}}{(X/Y)_{\text{Reference material}}} \quad (1)$$

where X is the total concentration of the considered trace element, Y is the concentration of the reference element (Al) and the Reference material is the deepest layer of the soil profile.

The underlying hypotheses of the EF method were that: (1) X and Y had the same behaviour in the soil column; (2) there were no anthropogenic sources of Y and (3) the reference material was not contaminated by X. EF = 2 was defined as the limit above which the studied sample was considered to be significantly enriched by an anthropogenic metal contamination, compared with the deepest horizon (Hernandez et al., 2003).

2.4.4. Principal component analysis (PCA)

PCA was performed on the composite soils data to visualise and to detect samples exhibiting high values of TMs. First, a scaling of the data was necessary. The Z-scores of the different parameters were calculated as follows (Eq. (2)):

$$Z - \text{scores} = \frac{X_i - m}{sd} \quad (2)$$

with X_i = value of the parameter X in the sample i; m = mean of X; sd = standard deviation of X.

The PCA was run with a varimax rotation that maximises the sum of the variances of the squared loadings. The graphical representation of the individual Z-scores on the principal components associated to the

Table 2

Description of trace metal concentrations (mg kg⁻¹) in calcareous and non-calcareous samples from the composite collection (layers 1 and 2) and number of contaminated sites (>upper-whisker). sd = standard deviation; N = number of soil samples; IQR = Interquartile range; Upper-whisker = 3rd quartile + 1.5 × IQR. The baseline value (mean + 2 × sd) was calculated with the uncontaminated concentrations (<upper-whisker).

	Cd	Co	Cr	Cu	Mo	Ni	Pb	Sn	Tl	Zn
<i>Calcareous soils</i>										
Median	0.25	14.0	66.2	23.3	0.75	34.8	28.4	3.60	0.70	92.0
sd	0.14	4.6	16.4	6.1	0.32	11.7	8.5	0.83	0.16	23.8
N	85	85	85	85	85	85	85	43	85	85
IQR	0.26	5.9	18.3	8.4	0.50	16.6	12.9	1.01	0.19	38.2
Maximum	2.41	72.8	118	268	4.85	64.1	150	5.61	1.75	444
Baseline value	0.55	22.8	95.4	34.9	1.39	58.5	46.8	5.21	1.00	135
Upper whisker	0.82	25.0	98.7	39.4	1.75	66.8	57.0	5.47	1.09	168
Sites > upper whisker	9	1	2	5	4	0	8	1	6	9
<i>Non-calcareous soils</i>										
Median	0.13	10.2	49.0	19.0	0.62	18.0	27.1	3.13	0.56	62.8
sd	0.10	6.0	19.0	9.9	0.26	9.9	8.2	0.97	0.19	28.2
N	117	117	117	117	117	117	117	65	117	117
IQR	0.15	9.3	28.5	16	0.40	15.3	12.1	1.73	0.29	42.1
Maximum	1.08	39.6	146	124	4.31	94.1	186	26.2	2.46	211
Baseline value	0.37	23.2	87.8	39.3	1.19	39.2	44.2	5.02	0.93	121
Upper whisker	0.47	30.4	106	51.8	1.50	50.3	53.0	6.68	1.16	150
Sites > upper whisker	3	4	4	7	4	6	5	5	9	5
<i>RMQS (composite 0–30 cm) national data (Villanneau et al., 2008)</i>										
Upper whisker	0.63	25.2	111	40.2	1.57	56.8	62.3	na	1.36	157.5

Table 3
Multiple linear regressions determined in deep horizons of calcareous and non-calcareous soils. Trace metal concentrations are in $\mu\text{g kg}^{-1}$ and semi-conservative elements used as predictors (Al, Fe, Mg, Mn, and Na) are in mg kg^{-1} . Significance levels: 0 < *** < 0.001 < ** < 0.01 < * < 0.05 < ns. Low or non-significant relationships are written in italics.

Model (for calcareous soils)	N	R ² _{adj}	p-Value
$\ln(\text{As}) = 0.47 \times \ln(\text{Al}) + 0.77 \times \ln(\text{Mn}) - 0.66$	19	0.91	1.2 ^{E-09} ***
$\ln(\text{Cd}) = 0.26 \times \ln(\text{Al}) + 0.62 \times \ln(\text{Mg}) - 3.11$	20	0.54	5.5 ^{E-04} ***
$\ln(\text{Co}) = 0.95 \times \ln(\text{Fe}) - 0.56$	23	0.93	6.9 ^{E-14} ***
$\ln(\text{Cr}) = 0.51 \times \ln(\text{Fe}) + 0.36 \times \ln(\text{Al}) + 0.13 \times \ln(\text{Mg}) + 0.63$	19	0.99	8.1 ^{E-16} ***
$\ln(\text{Cu}) = 0.83 \times \ln(\text{Fe}) + 0.26 \times \ln(\text{Mg}) - 1.15$	23	0.93	1.3 ^{E-12} ***
$\ln(\text{Mo}) = 0.32 \times \ln(\text{Na}) + 0.36 \times \ln(\text{Fe}) + 0.18$	19	0.71	1.9 ^{E-05} ***
$\ln(\text{Ni}) = 0.49 \times \ln(\text{Fe}) + 0.47 \times \ln(\text{Mg}) + 1.07$	22	0.72	2.3 ^{E-06} ***
$\ln(\text{Pb}) = 0.49 \times \ln(\text{Al}) + 0.63 \times \ln(\text{Mn}) + 0.50$	21	0.90	4.7 ^{E-10} ***
$\ln(\text{Sb}) = 0.82 \times \ln(\text{Mn}) - 0.23 \times \ln(\text{Al}) + 4.46$	19	0.48	2.2 ^{E-03} **
$\ln(\text{Sc}) = 0.46 \times \ln(\text{Fe}) + 0.44 \times \ln(\text{Mg}) + 0.71$	22	0.86	2.6 ^{E-09} ***
<i>$\ln(\text{Se}) = 0.39 \times \ln(\text{Na}) + 4.38$</i>	15	0.36	0.011 *
$\ln(\text{Sn}) = 0.79 \times \ln(\text{Al}) + 0.15 \times \ln(\text{Na}) - 1.75$	20	0.90	1.6 ^{E-09} ***
$\ln(\text{Tl}) = -0.52 \times \ln(\text{Fe}) + 0.99 \times \ln(\text{Al}) + 0.52 \times \ln(\text{Mn}) - 2.66$	22	0.94	1.0 ^{E-11} ***
$\ln(\text{V}) = 0.90 \times \ln(\text{Al}) + 1.39$	19	0.95	5.4 ^{E-13} ***
$\ln(\text{Zn}) = 1.46 \times \ln(\text{Fe}) - 0.71 \times \ln(\text{Al}) - 0.30 \times \ln(\text{Mn}) + 6.12$	21	0.86	5.6 ^{E-08} ***
Model (for non-calcareous soils)	N	R ² _{adj}	p-Value
$\ln(\text{As}) = 0.45 \times \ln(\text{Mn}) + 0.88 \times \ln(\text{Al}) - 3.00$	29	0.32	0.0028 **
<i>$\ln(\text{Cd}) = 0.46 \times \ln(\text{Mn}) + 0.43 \times \ln(\text{Na}) - 1.82$</i>	27	0.21	0.023 *
$\ln(\text{Co}) = 0.53 \times \ln(\text{Mn}) + 0.13 \times \ln(\text{Fe}) + 0.17 \times \ln(\text{Mg}) + 3.20$	32	0.79	3.4 ^{E-10} ***
$\ln(\text{Cr}) = 0.69 \times \ln(\text{Fe}) + 3.62$	27	0.41	2.0 ^{E-04} ***
$\ln(\text{Cu}) = 0.78 \times \ln(\text{Al}) + 0.29 \times \ln(\text{Mg}) - 1.38$	33	0.46	3.2 ^{E-05} ***
<i>$\ln(\text{Mo}) = -0.37 \times \ln(\text{Mg}) + 9.44$</i>	27	0.08	0.085 ns
$\ln(\text{Ni}) = 0.43 \times \ln(\text{Fe}) + 0.33 \times \ln(\text{Al}) + 1.82$	29	0.47	1.1 ^{E-04} ***
$\ln(\text{Pb}) = 0.27 \times \ln(\text{Mn}) + 8.29$	29	0.27	0.0016 **
<i>$\ln(\text{Sb}) = 0.22 \times \ln(\text{Mn}) + 6.05$</i>	25	0.02	0.23 ns
$\ln(\text{Sc}) = 0.41 \times \ln(\text{Fe}) + 0.48 \times \ln(\text{Al}) - 0.31$	31	0.52	1.2 ^{E-05} ***
<i>$\ln(\text{Se}) = -0.73 \times \ln(\text{Na}) + 13.11$</i>	18	0.04	0.20 ns
$\ln(\text{Sn}) = 0.92 \times \ln(\text{Al}) - 2.02$	27	0.48	4.0 ^{E-05} ***
$\ln(\text{Tl}) = 0.64 \times \ln(\text{Al}) + 0.13 \times \ln(\text{Mn}) - 1.62$	30	0.38	6.1 ^{E-04} ***
$\ln(\text{V}) = 0.95 \times \ln(\text{Fe}) + 1.42$	27	0.74	6.2 ^{E-09} ***
$\ln(\text{Zn}) = 0.48 \times \ln(\text{Fe}) + 0.19 \times \ln(\text{Mg}) + 4.70$	29	0.69	9.4 ^{E-08} ***

TM contents allowed the visualisation of anomalous TM concentrations. An arbitrary limit (for instance, z-score > 1) was set to discriminate the contaminated points from the investigated soil population.

3. Results

3.1. Trace metal background concentrations

3.1.1. Descriptive statistics (upper-whisker method)

The descriptive statistical parameters were calculated for Cd, Co, Cr, Cu, Mo, Ni, Pb, Sn, Tl and Zn concentrations in the composite samples of

both soil groups (Table 2). Regarding the global TM abundance in the studied soils, Co, Cu, Ni and Pb were of the same order of magnitude, whereas the concentrations were higher for Cr and Zn, lower for Sn, Mo and Tl and much lower for Cd. After the Kruskal–Wallis tests, the median concentrations of most TMs were found to be significantly higher in the calcareous soils than in the non-calcareous soils, except Pb (p = 0.069) and Sn (p = 0.056). However, the baseline values, calculated after the removal of concentrations above the upper-whisker, were higher in calcareous soils only for Cd, Ni, Zn and Mo. The variability was slightly higher in non-calcareous soils, as shown by the higher standard deviations for most TMs.

Table 4
Theoretical trace metal background concentrations (mg kg^{-1}) calculated in composite samples of calcareous and non-calcareous soils of the Midi-Pyrénées region (SW France) using the linear models developed in this study (see Table 3). The values were compared with background levels from the literature (na = not available).

	This study		Literature data		
	Calcareous	Non-calcareous	Sterckeman et al. 2006b ^a	Guillén et al. 2011 ^b	Baize, 2000 ^c
As	6–43	3–57	8.3	8.45 ± 1.03	na
Cd	0.07–0.54	0.04–0.34	0.11	0.13 ± 0.02	0.16
Co	4–21	3–47	10.1	9.72 ± 0.73	14.0
Cr	26–92	19–96	62	45.2 ± 6.8	66.3
Cu	6–40	2–48	11	17.6 ± 2.7	12.8
Mo	0.27–0.83	0.34–1.05	0.47	na	na
Ni	12–70	8–37	23.8	24.2 ± 2.3	31.0
Pb	10–56	15–41	16.2	26.8 ± 8.8	34.1
Sb	0.9–6.2	1.2–2.8	0.47	0.33 ± 0.07	na
Sc	5–26	3–18	na	na	na
Se	0.9–2.4	0.3–3.2	0.14	0.16 ± 0.06	na
Sn	1.6–4.6	1.0–5.6	1.72	1.52 ± 0.62	na
Tl	0.3–0.98	0.20–0.94	0.43	0.13 ± 0.02	na
V	45–123	21–195	69	49.7 ± 5.8	na
Zn	46–179	30–140	48	47.2 ± 2.4	80

^a Median values in deep horizons of sedimentary soils from northern France.

^b Mean ± standard deviation of background levels in sedimentary soils of Huelva municipality (SW of Spain).

^c Median values in various uncontaminated arable and forest soils throughout France.

3.1.2. Predicting models of natural concentrations of TMs

The linear models computed in the deep horizon of the calcareous and non-calcareous soils on the basis of relationships with Al, Fe, Mn, Mg and/or Na are shown in Table 3. The significance of the regressions varied according to the soil group and to the considered TM. The models were globally more significant in calcareous, than in non-calcareous soils, because of the better homogeneity of the bedrock in the former soil group. Among the considered TMs, Co, V and Zn were very well predicted by the models in both soil groups. The relationships were very significant in calcareous soils but less significant in non-calcareous soil for As, Cr, Cu, Mo, Ni, Pb, Sn and Tl. The regression for Mo in non-calcareous soils was not significant. Finally, natural concentrations of Cd, Sb and Se were less well predicted in all

soil types. Cd, Sb and Se showed very poor correlations with Fe or Al while these two major elements were often the best predictors of other TM concentrations. Cd and Sb were indeed preferably correlated to Mn. However, at high Fe ($>70 \text{ g kg}^{-1}$), Al ($>88 \text{ g kg}^{-1}$) and Mn ($>1.5 \text{ g kg}^{-1}$) concentrations, the relationships were not linear for several TMs. Thus, the limit of validity for the determination of the linear models was set below these concentrations.

Thanks to these linear models established in the deep layers, the theoretical TM concentrations in the composite samples were calculated following the observed concentrations of Fe, Al, Mn, Mg or Na (Table 4). As a result, the ranges of predicted TM concentrations reflected the variability of the major elements concentrations between sites. However, our results were consistent with previous

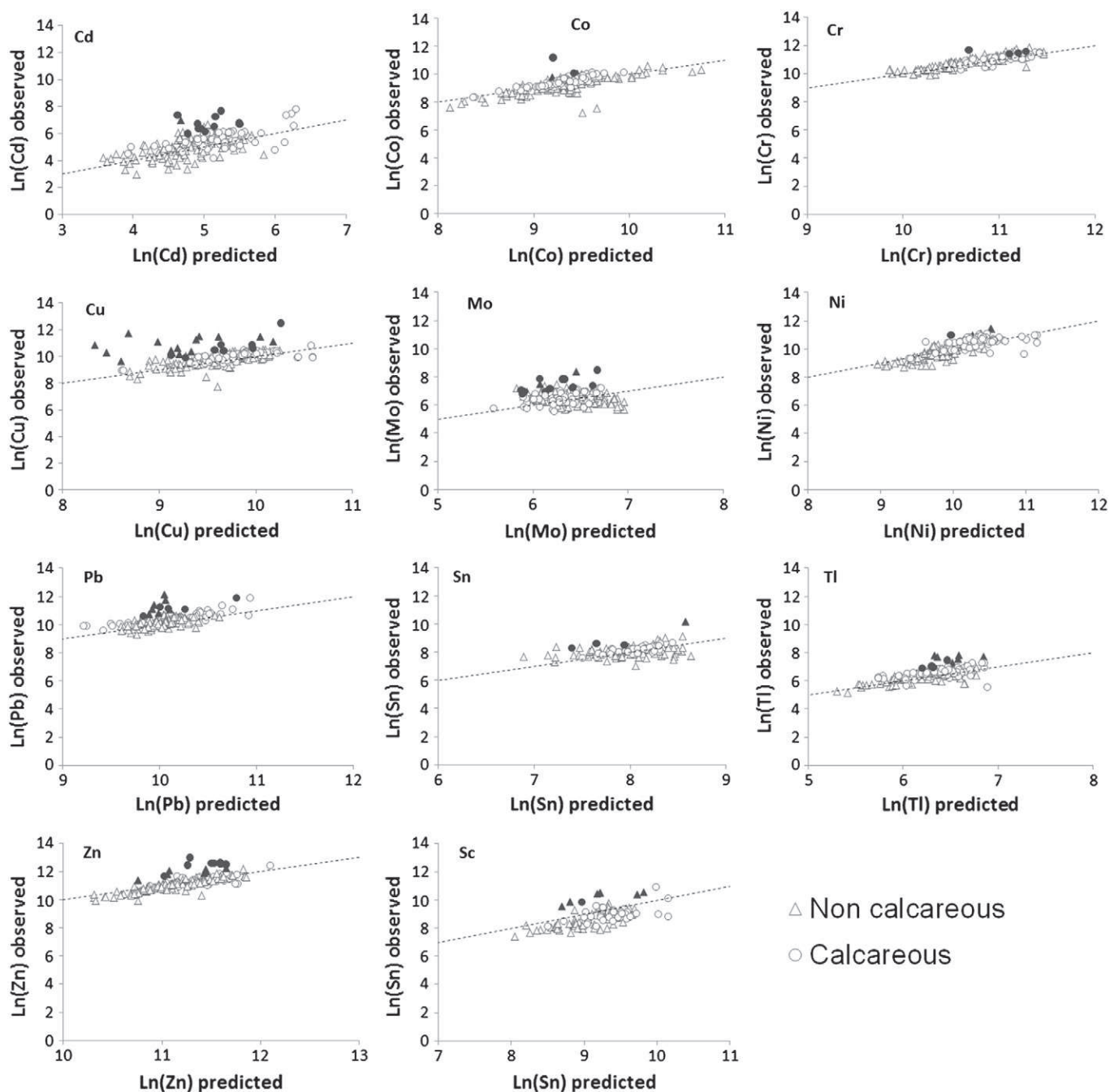


Fig. 3. Observed vs. predicted trace metal concentrations in composite soil samples. Concentrations ($\mu\text{g kg}^{-1}$) are ln-transformed. Calcareous samples are represented by circles and non-calcareous samples by squares. Black symbols are the observed values above the 95% predicted interval computed from the regression analysis in the deep horizons of the profiles collection. Dashed line is the 1:1 line.

studies and the baseline values calculated using the descriptive statistics corresponded to the higher values of the predicted ranges. The median theoretical concentrations of most TMs (except As, Co, Mo, Sb and Sn) were also significantly higher in calcareous soils than in non-calcareous soils.

3.2. Estimation of trace metal contaminations

3.2.1. Upper-whisker value

The upper-whisker value is a good descriptor of the TM levels in both soil groups of the studied region. The values of Cd, Mo, Ni, Pb and Zn were higher in calcareous soils than in non-calcareous soils, whereas it was the contrary for Co, Cr, Cu and Sn (Table 2). The upper-whisker values of the Midi-Pyrénées region were also globally similar to the values on the national scale (Villanneau et al., 2008). The proportion of anomalous concentrations (> upper-whisker) in the studied samples was the highest for Cd (10.6%), Zn (10.6%) and Pb (9.4%) in calcareous soils. A significant number (>5%) of anomalous levels were also found for Cu and Tl in both soil groups and for Tl and Ni in non-calcareous soils. Little contamination by Co, Cr and Mo was revealed with this method.

3.2.2. Observed vs. theoretical concentrations

The theoretical concentrations estimated by linear regression analysis were computed with a 95% prediction interval, which was defined as the decision limit for anomalous concentrations (Figure 3). A majority of the samples found to be out of the theoretical concentration limit for one or several of the studied TMs were from the surface horizon (0–30 cm) indicating superficial contamination, even if the horizon below (30–50 cm) was also affected in some sites, especially by Cu, Pb, Tl and Zn. The observed concentrations exceeded frequently the prediction limit for Cu, Mo, Zn, Cd and Pb. Fewer sites (<5%) were concerned by values above the limit for Tl, Cr, Sn, Co and Ni (Figure 3). According to the considered TM, there were also differences between calcareous and non-calcareous soils. Most contaminations were indeed observed in calcareous soils, except for Cu and Ni.

3.2.3. Enrichment factor

The EF calculation was based on the median values of the TM/Al ratios in the deepest layer of the profiles. The TM/Al ratios calculated for Cd, Cr, Ni and Zn were significantly higher (Kruskal–Wallis test; $p < 0.05$) in calcareous soils than in non-calcareous soils, while there was no significant differences for the other TMs studied (Table 1). A box-plot representation of the EF calculated for the composite samples is shown in Fig. 4. The median EF values varied between 1 and 2 for all TMs, even if a large variability was found for Cd. The EF was generally slightly higher in the 0–30 cm layer than in the 30–50 cm layer. Several samples exhibiting an EF above 2 were considered as anomalous values. Among these enriched samples, the soils were mainly contaminated by Cd (54% of the sites), Pb (28%), Cu (20%), Mo (18%) and Co (15%). Contamination by the other metals was less frequent (less than 10%). Few samples were very enriched in TMs ($EF > 5$) and this mainly concerned Cd, Cu and Pb contamination. The worst cases were two heavy loads of Cu in two surface soils ($EF = 23$ in both soils).

3.2.4. Principal component analysis

PCA was applied to the whole composite soil dataset (layers 1 and 2), except for Sn concentrations because many values were missing. A low variance (43%) was explained by the first four principal components (PCs). Due to the large number of soil properties in the dataset, the PCA analysis resulted in 16 PCs explaining 89% of the total variance. The 1st PC (12% of variance) was related to Cd, Zn and Pb total and EDTA-extractable concentrations, suggesting an influence on the dataset of a common contamination by these three metals. The 2nd

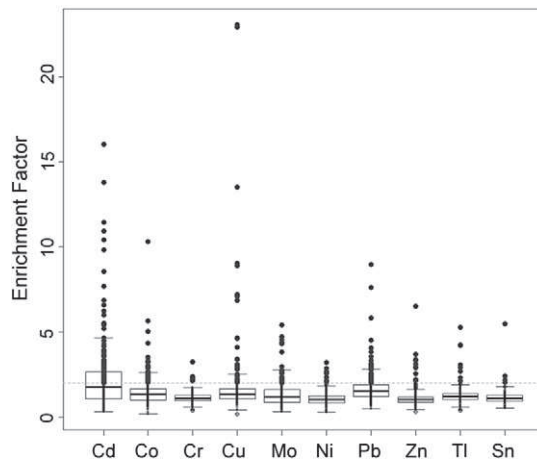


Fig. 4. Box-plot representation of the enrichment factor (EF) of trace metals (Cd, Co, Cr, Cu, Mo, Ni, Pb, Zn and Tl) calculated for the composite samples of the studied soils with the median TM/Al ratio in deep layer used as a reference. The samples enriched in TM compared with the deep horizon ($EF > 2$) are identified by black points.

PC (12%) was related to the total Fe, Al and Mn concentrations associated with the Cr, Co and Ni total contents. The 3rd PC (11%) was related to the cationic exchange capacity (CEC), exchangeable Ca, pH, clay and water content and the 4th PC (8%) to the organic matter content. The 7th PC (5%) was also of interest because it was related to the total and extractable Cu concentrations, suggesting an influence of Cu contamination. A graphical representation of the individual scores in the PC1 (Cd, Zn, and Pb) versus PC3 allowed the identification of samples contaminated by those three metals (7.4% of the samples; Figure 5A). The Cu-contaminated samples (4.9%) were identified similarly, using the PC7 vs. PC3 (Figure 5B). Score values above 1 were arbitrary defined as contaminated samples. We also identified the sites contaminated by Tl (3.9% of the samples) and Mo (3.0%) using the PC6 (5% of variance) and the PC15 (2%), respectively (values above 2 in this case, data not shown).

3.2.5. Soil contamination according to the different methods: link to land use

The four methods applied on the scale of a French region to estimate the anomalous TM concentrations showed some differences, even though the results were globally consistent (Figure 6). For at least three methods, roughly the same contaminated sites with the same TM contaminants were identified, while the enrichment factor method detected a greater number of anomalous concentrations than the other methods. The contaminations concerned mostly Cd, Cu, Mo, Pb, Tl and Zn (Table 5) and tended to be more numerous in the north-eastern part of the region (Figure 6). More numerous cases of contamination were also observed in calcareous than in non-calcareous soils (Table 5).

The anomalous TM concentrations detected by at least three out of the four methods can reasonably be considered as very probably contaminated and a representation of these sites on a synthetic map (Figure 6E) provides a good evaluation of the soil quality in the studied region. The diagnosis of this approach was that 30 sites (24%) had a high probability of contamination by at least one TM. Additional sites also presented a non-negligible risk of being contaminated because they were detected by half of the applied methods. Taking these sites into account raised the proportion of contaminations up to 37%. Several single Cu contaminations (6.5% of the studied sites) occurred in current or former vineyards and orchards and multi-metallic contaminations (mainly by Cd, Pb and Zn in 6.5% of the studied sites) were found mostly in grasslands used for intense livestock farming. Additionally, a few single contaminations by Mo, Cd or Pb were also identified in various land uses whereas thallium, nickel, chromium,

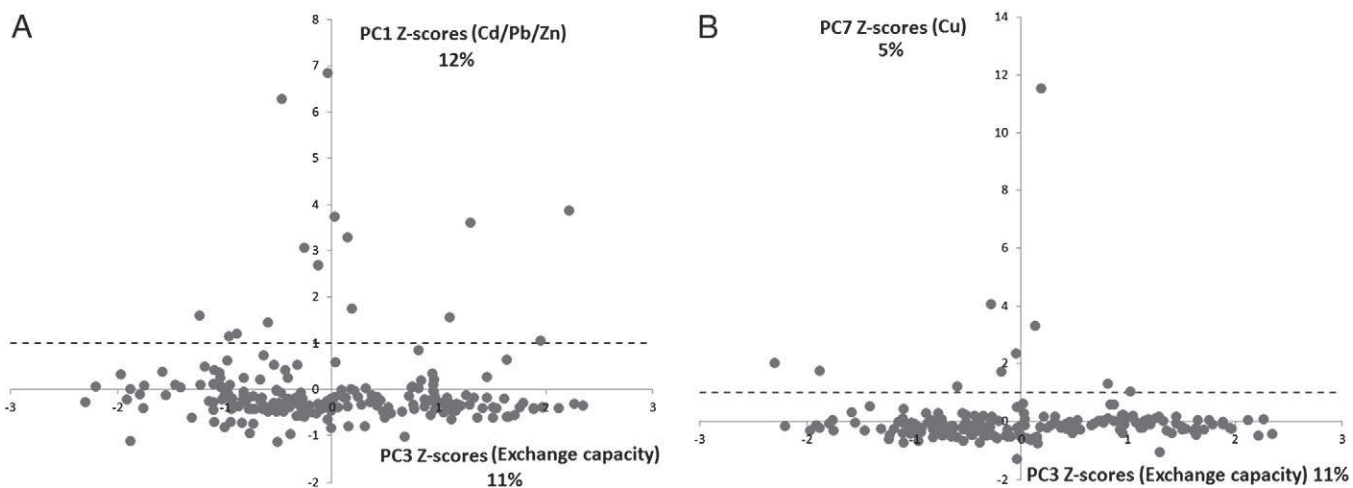


Fig. 5. Score plots of (A) principal component 1 (PC1) versus PC3 and (B) PC8 versus PC3. The dashed line represents the limit value above which the sample is considered to be contaminated by Cd, Pb and/or Zn (A) or Cu (B).

cobalt and tin contaminations were rare and concerned only grasslands. Thus, globally, croplands other than vineyards and orchards were barely affected by anomalous TM concentrations.

4. Discussion

4.1. Comparison of the different methods of estimating soil metal background and contaminations

The comparison of the methods used in our study may help to choose the soil contamination assessment method that is the most appropriate to a particular case study, depending on the objectives and on the environment and contaminants involved. The reliability of soil contamination assessment methods has been questioned (Desaules, 2012) because all methods rely on assumptions of reference values for natural content that can show some discrepancies due to the great variability of soil properties and to the processes that can redistribute the elements within the soil column. Local ranges of natural background concentrations of TMs must indeed be well defined for an accurate evaluation of soil contamination.

As a first approach, the baseline values and the upper-whisker limit given by descriptive statistics are good indicators of the ambient levels recorded in a local soil population. They are easy to compute and give a rapid view of the metal levels in the different soil groups classified, prior to performing the calculations. The upper-whisker method seems to be the best approach to assess the contaminations for the most mobile elements, like Cd, which are difficult to model. Nevertheless, these descriptive parameters also reflect diffuse contaminations that are difficult to discriminate from the geochemical background. Moreover, without a sound knowledge of the geological context, natural anomalies can be misinterpreted as true contaminations. As a result, this method should not be applied where high diffuse contaminations are suspected or where local natural anomalies can occur.

The elaboration of predicting models based on the linear relationships between the natural TMs and the major elements constitutive of the soil minerals can partly help overcome these limitations. Theoretical natural concentrations can indeed be estimated by taking into account the variability of the soil processes, thanks to the good relationships of some TMs with elements, such as Fe, Al and Mn. Indeed these concentrations are related more to the chemical composition of the parent material and to the degree of weathering than

to the anthropogenic influence (Zhao et al., 2007). As these geochemical associations differ significantly across the different soil orders (Anderson and Kravitz, 2010), this method should be applied to larger datasets with a detailed classification in more than two soil groups, in order to build models that are more robust than in our case study. However, some TMs, especially the most mobile ones, are not well correlated to the major elements and this can lead to high uncertainties in the calculation of the theoretical concentrations.

According to these two methods, a large number of samples are necessary to obtain good estimates of the TM background concentrations but such extensive soil monitoring programmes may not be available or may not fit with targeted objectives. The enrichment factor method was widely used as a geochemical method to determine whether a soil sample is abnormally enriched in a considered TM or not. This method only needs to know the TM local reference value (normalised or not) in order to assess the contamination of a sample. This is of great advantage for studies with only a few single analyses. Nevertheless, uncontaminated local reference values can be difficult to obtain and the soil processes involved in the reference material may not be exactly the same as in the studied sample. This will lead to bias, especially when considering TMs at low concentrations, like Cd. Nevertheless, the enrichment factor remains a good tool for the identification of intense local contamination but cannot be generalised over large areas or for sample sites far from a likely contamination source (Reimann and de Caritat, 2005).

Multivariate analysis was the final method applied in this study to graphically identify the anomalous points. The PCA allowed the information contained in a complex database to be simplified and to highlight the major processes influencing TM concentrations. It is a good tool in preliminary surveys for the identification of sites affected by the same contamination sources and of the TMs involved in the contamination (Facchinelli et al., 2001). For instance, the PCA showed that Cd together with Pb and Zn and Cu alone, are controlled by anthropic activities, whereas Cr, Co and Ni were mainly controlled by parent rocks. However, this method allows only an arbitrary estimation of the highest contaminations, because it does not provide a decision limit set on a mathematical or statistical basis.

For all the tested methods the decision limit was the key parameter that defined whether a site was contaminated or close to the natural background. Due to the large variability generally encountered in soil studies and to the diffuse contaminations, the chosen limit may not reflect the actual natural background concentrations.

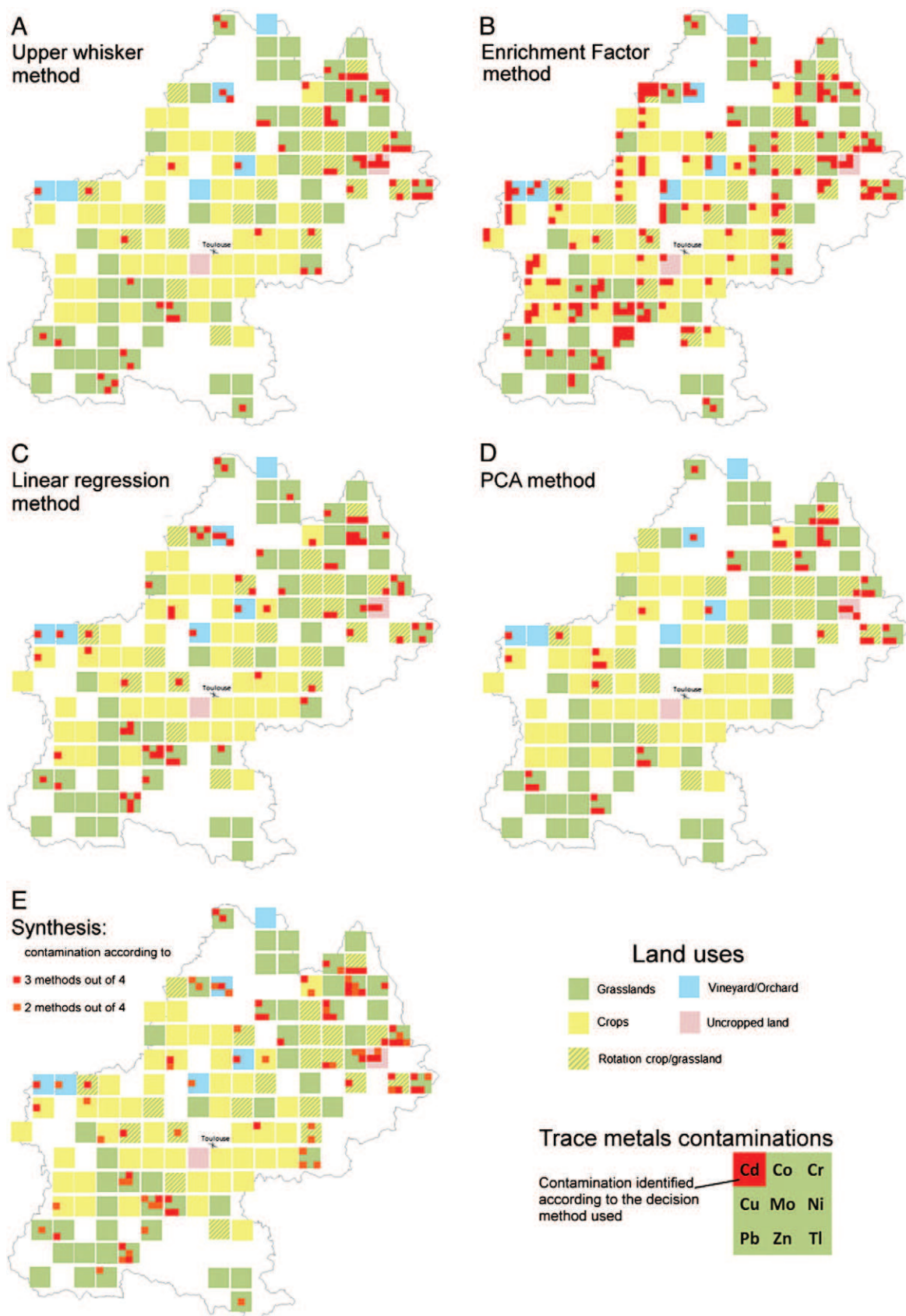


Fig. 6. Maps of metal contaminated sites in the sampled area (Midi-Pyrénées region, France) identified using four decision tools (A to D; see text for the details of the methods). Each square corresponding to a sampling site is coloured according to its land use. Within these squares, a contamination by one of the 9 trace metals (Cd, Co, Cr, Cu, Mo, Ni, Pb, Zn and Tl) is figured in red following the position of the metal on the square. Figure E synthesises the results of the four methods. It represents the sites found contaminated by at least 3 methods out of 4 (in red) and by 2 methods out of 4 (in orange).

Table 5

Proportion (%) of contaminated sites (layer 1 of composite samples) identified following the four decision tools used in this study (ND: not determined).

%	Cd	Co	Cr	Cu	Mo	Ni	Pb	Sn	Tl	Zn
<i>Upper-whisker method</i>										
All	8.1	2.4	4.1	7.3	4.9	3.3	8.9	4.9	7.3	8.1
Calcareous	13.7	2.0	3.9	7.8	5.9	0.0	13.7	2.3	9.8	13.7
Non-calcareous	4.2	2.8	4.2	6.9	4.2	5.6	5.6	7.7	5.6	4.2
<i>Enrichment factor method</i>										
All	53.7	14.6	3.3	20.3	17.9	4.9	27.6	4.6	4.1	6.5
Calcareous	45.1	3.9	2.0	13.7	27.5	3.9	27.5	4.6	5.9	13.7
Non-calcareous	59.7	22.2	4.2	25.0	11.1	5.6	27.8	4.6	2.8	1.4
<i>Linear regression method</i>										
All	8.9	2.4	3.3	13.0	10.6	2.4	6.5	3.7	4.1	9.8
Calcareous	19.6	3.9	7.8	13.7	21.6	2.0	7.8	7.0	5.9	13.7
Non-calcareous	1.4	1.4	0.0	12.5	2.8	2.8	5.6	1.5	2.8	6.9
<i>PCA method</i>										
All	9.8	ND	ND	6.5	3.3	ND	9.8	ND	3.3	9.8
Calcareous	17.7	ND	ND	5.9	5.9	ND	17.7	ND	0	17.7
Non-calcareous	4.2	ND	ND	6.9	1.4	ND	4.2	ND	5.6	4.2

Consequently, several methods should be compared together in order to give a coherent conclusion regarding the contamination state of a site.

4.2. Intensity of site contamination: role of soil characteristics and potential sources from agricultural practices

Modelling the background concentrations showed that natural TMs were preferentially related to Fe, Al and Mn, the major constituents of oxides and clays (Sparks, 2003) and were poorly correlated to Ca, suggesting that oxides and clays are the main TM bearing phases. However, the properties (especially pH) of calcareous soils may lead to the immobilisation of TMs in soils because metals are usually less mobile at alkaline pH. This may explain the highest TM concentrations (both natural and anthropogenic) observed in calcareous soils compared with acidic soils, where the TMs are more likely to be leached or taken up by plants. The low mobility of TMs in calcareous soils may favour the accumulation of contaminants in soils because more cases of TM contamination were detected in calcareous than in non-calcareous soils. Such difference between calcareous and non-calcareous soils was not related to a preferential land use since crops were almost equally distributed on both soil types, and grasslands were twice more frequent on non-calcareous than on calcareous soils. The intensity and the nature of contamination were however strongly influenced by agricultural practices. The frequent anomalous Cu concentrations in vineyards and orchards indeed reflected the application of copper-based fungicides (the “Bordeaux mixture”, CuSO_4) as primary sources of Cu contaminations (Komárek et al., 2008; Viti et al., 2008) and the multi-metallic (Cd, Pb and Zn) contaminations reported in grazing lands suggested that the animal effluents and all potential organic fertilisers (solid wastes and sewage sludge) applied to soils are the major causes of TM enrichment. These dominant sources of contamination are not exclusive, because a few single Mo, Cd and Pb contaminations were also detected even though their origins cannot be clearly identified.

Finally, in the studied area, the revealed contaminations were generally low compared with industrial regions, e.g., in the north of France and close to Paris (Saby et al., 2011). Except in a few sites (Cu in vineyard/orchard and Pb/Zn/Cd contaminations in some grasslands), the TM concentrations were indeed below the French limits above which sewage sludge cannot be applied (in mg kg^{-1} : Cd 2; Cr 150; Cu 100; Hg 1; Ni 50; Pb 100; Se 10; and Zn 300).

5. Conclusion

The geochemical background can be well modelled by multiple linear regression using elements (especially Fe and Al) constitutive of soil minerals, showing that natural TM concentrations mostly derive from mineral weathering. However, the most mobile elements were poorly modelled and alternatively, basic descriptive statistics can be used to estimate the natural levels of such elements in soils. Following both methods of TM background determination, several TMs were found to be naturally more abundant in calcareous than in non-calcareous soils, maybe because of a lower TM mobility at alkaline pH. The low mobility of TMs in calcareous soils may also favour the accumulation of contaminants in soils because more cases of TM contamination were detected in calcareous than in non-calcareous soils. The sources of contamination were multiple and dependent of the land-use history. However, none of the four methods used to estimate the fraction of exogenous TMs in the soils of the studied region was perfect and universal. Thus, our study emphasises the need to use several methods in order to be able to draw the best conclusion regarding the contamination status of a site. A combination of the decision tools used in this study showed that 24% of the agricultural soils of the Midi-Pyrénées region of France were contaminated by at least one TM. However, relatively low levels of contamination were measured and this predominantly concerned Cu, Cd, Pb and Zn. Copper contamination was mainly found in vineyards and orchards because of the long-term application of fungicides (the “Bordeaux mixture”), while livestock breeding was the major cause of multi-contamination by Cd, Pb and Zn in grasslands.

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References

- Amiotte-Suchet, P., Probst, J.-L., Ludwig, W., 2003. Worldwide distribution of continental rock lithology: implications for the atmospheric/soil CO_2 uptake by continental weathering and alkalinity river transport to the oceans. *Global Biogeochemical Cycles* 17, 1038–1051.
- Anderson, R.H., Kravitz, M.J., 2010. Evaluation of geochemical associations as a screening tool for identifying anthropogenic trace metal contamination. *Environmental Monitoring and Assessment* 167, 631–641.
- Baize, D., 2000. Teneurs totales en “métaux lourds” dans les sols français. Résultats généraux du programme ASPITET. *Le Courrier de l'Environnement de l'INRA* 39, 39–54. <http://www.inra.fr/dpenv/baizec39.htm> (in french).
- Baize, D., Girard, M., 2009. Référentiel pédologique 2008. AFES, Editions Quae, Paris.
- Baize, D., Sterckeman, T., 2001. Of the necessity of knowledge of the natural pedo-geochemical background content in the evaluation of the contamination of soils by trace elements. *Science of the Total Environment* 264, 127–139.
- Bini, C., Sartori, G., Wahsha, M., Fontana, S., 2011. Background levels of trace elements and soil geochemistry at regional level in NE Italy. *Journal of Geochemical Exploration* 109, 125–133.

- Candeias, C., Ferreira da Silva, E., Salgueiro, A.R., Pereira, H.G., Reis, A.P., Patinha, C., Matos, J.X., Ávila, P.H., 2010. The use of multivariate statistical analysis of geochemical data for assessing the spatial distribution of soil contamination by potentially toxic elements in the Aljustrel mining area (Iberian Pyrite Belt, Portugal). *Environmental Earth Sciences* 62, 1461–1479.
- Chester, R., Stoner, J.H., 1973. Pb in particulates from the lower atmosphere of the eastern Atlantic. *Nature* 245, 27–28.
- Desaules, A., 2012. Critical evaluation of soil contamination assessment methods for trace metals. *Science of the Total Environment* 426, 120–131.
- Facchinelli, A., Sacchi, E., Mallen, L., 2001. Multivariate statistical and GIS-based approach to identify heavy metal sources in soils. *Environmental Pollution* 114, 313–324.
- Fleischhauer, H.L., Korte, N., 1990. Formulation of cleanup standards for trace elements with probability plots. *Environmental Management* 14, 95–105.
- Gil, C., Boluda, R., Ramos, J., 2004. Determination and evaluation of cadmium, lead and nickel in greenhouse soils of Almería (Spain). *Chemosphere* 55, 1027–1034.
- Guillén, M.T., Delgado, J., Albanese, S., Nieto, J.M., Lima, A., De Vivo, B., 2011. Environmental geochemical mapping of Huelva municipality soils (SW Spain) as a tool to determine background and baseline values. *Journal of Geochemical Exploration* 109, 59–69.
- Hamon, R.E., McLaughlin, M.J., Gilkes, R.J., Rate, A.W., Zarcinas, B., Robertson, A., Cozens, G., Radford, N., Bettenay, L., 2004. Geochemical indices allow estimation of heavy metal background concentrations in soils. *Global Biogeochemical Cycles* 18 (Available at <http://www.agu.org/pubs/crossref/2004/2003GB002063.shtml> (verified 4 May 2012)).
- He, Z.L., Yang, X.E., Stoffella, P.J., 2005. Trace elements in agroecosystems and impacts on the environment. *Journal of Trace Elements in Medicine and Biology* 19, 125–140.
- Hernandez, L., Probst, A., Probst, J.L., Ulrich, E., 2003. Heavy metal distribution in some French forest soils: evidence for atmospheric contamination. *Science of the Total Environment* 312, 195–219.
- Komárek, M., Száková, J., Rohošková, M., Javorská, H., Chrástný, V., Balík, J., 2008. Copper contamination of vineyard soils from small wine producers: a case study from the Czech Republic. *Geoderma* 147, 16–22.
- Lafuente, A.L., González, C., Quintana, J.R., Vázquez, A., Romero, A., 2008. Mobility of heavy metals in poorly developed carbonate soils in the Mediterranean region. *Geoderma* 145, 238–244.
- Matschullat, J., Ottenstein, R., Reimann, C., 2000. Geochemical background – can we calculate it? *Environmental Geology* 39, 990–1000.
- Micó, C., Peris, M., Recatalá, L., Sánchez, J., 2007. Baseline values for heavy metals in agricultural soils in an European Mediterranean region. *Science of the Total Environment* 378, 13–17.
- Mrvić, V., Kostić-Kravljjanac, L., Čakmak, D., Sikirić, B., Brebanović, B., Perović, V., Nikoloski, M., 2011. Pedochemical mapping and background limit of trace elements in soils of Braničevo Province (Serbia). *Journal of Geochemical Exploration* 109, 18–25.
- N'guessan, Y.M., Probst, J.L., Bur, T., Probst, A., 2009. Trace elements in stream bed sediments from agricultural catchments (Gascogne region, S-W France): where do they come from? *Science of the Total Environment* 407, 2939–2952.
- Ouhadi, V.R., Yong, R.N., Shariatmadari, N., Saeidijam, S., Goodarzi, A.R., Safari-Zanjani, M., 2010. Impact of carbonate on the efficiency of heavy metal removal from kaolinite soil by the electrokinetic soil remediation method. *Journal of Hazardous Materials* 173, 87–94.
- Panichayapichet, P., Nitisoravut, S., Simachaya, W., 2007. Spatial distribution and transport of heavy metals in soil, ponded-surface water and grass in a Pb-contaminated watershed as related to land-use practices. *Environmental Monitoring and Assessment* 135, 181–193.
- Perrin, A.-S., Probst, A., Probst, J.-L., 2008. Impact of nitrogenous fertilizers on carbonate dissolution in small agricultural catchments: implications for weathering CO₂ uptake at regional and global scales. *Geochimica et Cosmochimica Acta* 72, 3105–3123.
- Plassard, F., Winiarski, T., Petit-Ramel, M., 2000. Retention and distribution of three heavy metals in a carbonated soil: comparison between batch and unsaturated column studies. *Journal of Contaminant Hydrology* 42, 99–111.
- Reimann, C., de Caritat, P., 2005. Distinguishing between natural and anthropogenic sources for elements in the environment: regional geochemical surveys versus enrichment factors. *Science of the Total Environment* 337, 91–107.
- Reimann, C., Filzmoser, P., Garrett, R.G., 2005. Background and threshold: critical comparison of methods of determination. *Science of the Total Environment* 346, 1–16.
- Roca, N., Pazos, M.S., Bech, J., 2008. The relationship between WRB soil units and heavy metals content in soils of Catamarca (Argentina). *Journal of Geochemical Exploration* 96, 77–85.
- Roussiez, V., Ludwig, W., Probst, J.-L., Monaco, A., 2005. Background levels of heavy metals in surficial sediments of the Gulf of Lions (NW Mediterranean): an approach based on ¹³³Cs normalization and lead isotope measurements. *Environmental Pollution* 138, 167–177.
- Saby, N.P.A., Thioulouse, J., Jolivet, C.C., Ratié, C., Boulonne, L., Bispo, A., Arrouays, D., 2009. Multivariate analysis of the spatial patterns of 8 trace elements using the French soil monitoring network data. *Science of the Total Environment* 407, 5644–5652.
- Saby, N.P.A., Marchant, B.P., Lark, R.M., Jolivet, C.C., Arrouays, D., 2011. Robust geostatistical prediction of trace elements across France. *Geoderma* 162, 303–311.
- Sparks, D., 2003. *Environmental Soil Chemistry*, 2nd ed. Academic Press, London.
- Steinnes, E., Allen, R.O., Petersen, H.M., Rambæk, J.P., Varskog, P., 1997. Evidence of large scale heavy-metal contamination of natural surface soils in Norway from long-range atmospheric transport. *Science of the Total Environment* 205, 255–266.
- Sterckeman, T., Douay, F., Baize, D., Fourrier, H., Proix, N., Schwartz, C., 2006. Trace elements in soils developed in sedimentary materials from Northern France. *Geoderma* 136, 912–929.
- Sterckeman, T., Douay, F., Baize, D., Fourrier, H., Proix, N., Schwartz, C., Carignan, J., 2006. Trace element distributions in soils developed in loess deposits from northern France. *European Journal of Soil Science* 57, 392–410.
- Tobias, F., Bech, J., Algarra, P., 1997. Establishment of the background levels of some trace elements in soils of NE Spain with probability plots. *Science of the Total Environment* 206, 255–265.
- Vijver, M.G., Spijker, J., Vink, J.P.M., Posthuma, L., 2008. Determining metal origins and availability in fluvial deposits by analysis of geochemical baselines and solid-solution partitioning measurements and modelling. *Environmental Pollution* 156, 832–839.
- Villanneau, E., Perry-Giraud, C., Saby, N., Jolivet, C., Marot, F., Maton, D., Floch-Barneaud, A., Antoni, V., Arrouays, D., 2008. Détection de valeurs anormales d'éléments traces métalliques dans les sols à l'aide du Réseau de Mesure de la Qualité des Sols. *Etude et Gestion des Sols* 15, 183–200.
- Viti, C., Quaranta, D., Philippis, R., Corti, G., Agnelli, A., Cuniglio, R., Giovannetti, L., 2008. Characterizing cultivable soil microbial communities from copper fungicide-amended olive orchard and vineyard soils. *World Journal of Microbiology and Biotechnology* 24, 309–318.
- Wilson, M.A., Burt, R., Indorante, S.J., Jenkins, A.B., Chiaretti, J.V., Ulmer, M.G., Scheyer, J.M., 2008. Geochemistry in the modern soil survey program. *Environmental Monitoring and Assessment* 139, 151–171.
- Yay, O.D., Alagha, O., Tuncel, G., 2008. Multivariate statistics to investigate metal contamination in surface soil. *Journal of Environmental Management* 86, 581–594.
- Zhao, F.J., McGrath, S.P., Merrington, G., 2007. Estimates of ambient background concentrations of trace metals in soils for risk assessment. *Environmental Pollution* 148, 221–229.