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Assessment and Use of Local Reference Values of Trace Metals in Topsoils. Application to a French Region

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Abstract

The French legislation for the management of potentially polluted sites requires that "the state of the soils of the site under study" be compared to the state of neighbouring natural soils. That is why diverse institutions try to find local data relating to trace metal concentrations in the soil (often called 'background values'), to use as points of comparison and thereby estimate the contamination level of the studied soil. However, in industrial or urban context, it is very difficult to find "natural soils" located in the vicinity. More often than not, these assessments can at best be carried out with reference to soils considered to be relatively little-contaminated, namely the closest agricultural soils. In France, a large data collection was carried out on a national scale. These data were provided by analyses made in ploughed topsoils, undertaken mainly within the framework of sewage sludge spreading plans. The data collected on the area of the region Centre have been processed and stratified according to "agricultural districts", territories much less heterogeneous from geological and pedological standpoints than administrative subdivisions. The usual measures of position (percentiles) and of dispersion (upper whiskers) have been determined for each agricultural district. These indicators may be used as appropriate reference values.

Introduction

New French legislation for the management of potentially polluted sites requires that "the state of the environment" (i.e. of the soils and waters of the industrial site under study) be compared to the state of neighbouring natural environments or to regulatory management values established by public authorities.

Within the framework of urban planning projects or conversion of former industrial sites, many studies are daily carried out in order to assess the risk to the population. Departments responsible for public health are recipients of these and must put forward an opinion. In the absence of statutory values, everyone tries to find local or regional data relating to trace metal concentrations in the soil (often called 'background values'), to use as points of comparison and thereby estimate the contamination level of the soil under study.

Unfortunately, in such an industrial or urban context, it is very difficult to find "natural soils" located in the vicinity, which are similar enough from a pedological standpoint. More often than not, these assessments can at best be carried out with reference to soils considered to be relatively little-contaminated, namely the closest agricultural soils.

The available data

In France, a large data collection was carried out on a national scale in 2009 (Duigou & Baize, 2010). These data were provided by analyses, undertaken mainly within the framework of sewage sludge spreading plans and of some research programmes. The samples were taken from surface horizons of ploughed soils. These analyses only involved Cd, Cr, Cu, Hg, Ni, Pb and Zn and were taken from more than 73,000 sites throughout France. These are the only data available in large numbers.

Due to their origins, (topsoil analyses from agricultural soils of various types), these analyses very largely correspond to "usual agricultural contents" i.e. natural pedogeochemical concentration + local additional contamination by farming practices and diffuse atmospheric deposition. These "usual agricultural contents" correspond to the lowest concentrations that it is possible to measure in an urban or peri-urban soil, close to an industrial site.

Application to the "Centre" region

The same approach was earlier applied to the "Ile de France" region (which encompasses the entire Paris area), although this was a simple case as there are no natural trace element anomalies. Once processed, the available data was used to provide health departments with trace metal threshold values for Paris area soils, beyond which one may suspect that some of the pollutants measured originated from the activity under study (Mathieu et al., 2008).

The main towns of the Centre region are Orléans, Tours, Chartres, Châteauroux, Blois and Bourges. This region (which covers 39,000 km²) displays a wide variety of parent rocks and therefore of soils. It is divided into "agricultural districts", territories which are used as a framework for agricultural statistics. These have been defined according to criteria of geology, landscape and type of agriculture. Consequently they constitute much less heterogeneous territories from geological and pedological standpoints than administrative subdivisions.

In the Centre region, two categories of natural trace metal anomalies are well-known: i) scattered Cd anomalies linked to Oxford limestone, situated in the agricultural district known as "Champagne-Berrichonne"; ii) Pb, Zn and Cd mineralizations of some rocks located in contact between sedimentary (Paris

basin) and cratonic domains (Massif Central). These mineralizations transmitted to the soils have been observed in the agricultural district called "Boischaud Sud". The national collection has allowed the contents of seven trace elements from 5913 sites throughout the region to be gathered.

The usual measures of position (percentiles) and of dispersion (upper whiskers) have been determined for each agricultural district. These indicators may be used as appropriate reference values. Two examples are discussed below. The first question is whether two relatively high values for Pb and Cd are to be considered as very probable contamination or whether these are among the usual values for the territory under study. This provides an initial idea of site contamination and therefore of the risk level to the environment or population. The risk must be then assessed more accurately using other methods such as partial extractions with neutral salts.

Example 1: a lead concentration of 80 mg/kg has been measured in topsoil. Such a value is much higher than the P95 and than the upper whisker of the region as a whole (Table 1). This concentration is also far higher than the P95 and the upper whisker of almost all the agricultural districts of the region. The only exception is for Boischaud Sud, whose P90 is precisely 80 mg/kg and P95 is 151 mg/kg. Of the 259 sites of Boischaud Sud, 26 measurements exceed 80 mg of Pb per kg and 13 exceed 151 mg/kg.

Example 2: a cadmium concentration of 0.80 mg/kg is much higher than the P95 and the upper whisker of the region as a whole. It is also much higher than the P95 and upper whiskers of almost all the agricultural districts except for Champagne-Berrichonne and Boischaud Sud.

When one needs to take up a position with reference to threshold values, which parameter should one choose: P90, P95 or the upper whisker? Why select one rather than another? Isn't the upper whisker more representative of the real population structure under study, especially when it comes to a narrow

interquartile range? However, selecting the 90 or 95 percentile means that one automatically considers that 5 or 10% of the values are anomalous or suspect.

Conclusions

As there is no better available way of obtaining usable and precise local reference values for usual trace metal concentrations, the 2009 national data collection is the only sufficiently abundant data source. Indeed, topsoil analyses are now available for more than 73,000 sites rather well-spread across French territory. These concentrations have been measured in ploughed horizons, which have received diffuse atmospheric fallout and diverse inputs linked to agricultural practices.

This collection provides objective points of comparison for any institution or consultancy office wishing to confront the results of an analysis with various statistical indicators to decide whether the measure is anomalous or not. If the available data are sufficiently numerous, these statistics generated stratifying by agricultural districts are the most pertinent.

Finally, the diagnosis as to whether a value is truly natural or anthropogenic will have to be based on a pedologically and geologically thorough point study of the site, without forgetting a historical inventory of possible sources of pollution.

References

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Mathieu A., Baize D., Raoul C. & Daniau C., 2008. Proposition de référentiels régionaux en éléments traces métalliques dans les sols : leur utilisation dans les évaluations des risques sanitaires. *Environnement, Risques & Santé*, vol 7, 2, pp. 112-122.

Table 1 Cadmium and lead percentiles and upper whiskers (UW) for three agricultural districts and the Centre region as a whole.

Cadmium - mg kg ⁻¹	N	P50	P75	P90	P95	UW
Centre region	5528	0.22	0.31	0.44	0.59	0.55
Beauce	923	0.28	0.32	0.37	0.44	0.45
Champagne Berrichonne	397	0.40	0.62	0.81	0.95	1.20
Boischaud Sud	239	0.25	0.36	0.70	0.98	0.63

Lead - mg kg ⁻¹	N	P50	P75	P90	P95	UW
Centre region	5893	22.0	27.6	34.4	39.3	43.8
Beauce	924	20.8	24.5	28.6	33.0	36.1
Champagne Berrichonne	405	27.2	32.8	38.3	41.1	47.8
Boischaud Sud	259	31.6	45.9	80.0	151.0	79.5