

Mercury content in topsoils, and geostatistical methods to identify anthropogenic input in the Ebro basin (Spain)

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Abstract

The sources of mercury (Hg) variability in agricultural soils have been evaluated using 624 soil samples that were taken in the northeast of Spain. The Hg concentration ranges were 1–717 $\mu\text{g kg}^{-1}$. This was a wide range, although 90% of the values for Hg contents were estimated between 2.5 and 70 $\mu\text{g kg}^{-1}$. Other soil parameters (the pH, organic matter, carbonates and particle size) showed little correlation with the Hg content. The anthropogenic influence was linked to specific practises, in particular the application of slurries. Maps of the spatial distribution indicated various areas with high concentration levels that are attributed to anthropogenic influences. Evidence of human activity can be seen in the Ebro delta, which reflects the accumulation of metals in the basin over many years, and on the Ebro headwaters, characterized by intense mining and smelting activities in the past. A significant portion of the increased Hg content in the Ebro valley probably comes from the deposition of anthropogenic atmospheric Hg due to emissions from industrial activities.

Additional key words: anthropogenic influences, heavy metals, kriging, spatial distribution, topsoils.

Resumen

Contenido superficial de mercurio en suelos del valle del Ebro: métodos geostadísticos para evaluar la influencia antrópica

En este trabajo se ha evaluado la variabilidad espacial en la concentración de mercurio (Hg) en suelos agrícolas utilizando 624 muestras recogidas en el noreste de España. Aunque se muestra un amplio rango en la concentración de Hg (1–717 $\mu\text{g kg}^{-1}$), el 90% de los valores varía entre 2,5 y 70 $\mu\text{g kg}^{-1}$. El contenido de Hg en suelos se ha visto ligeramente correlacionado con otros parámetros edáficos (pH, materia orgánica, carbonatos y textura). La influencia antropogénica en la concentración de Hg en suelos se ha visto ligada a prácticas agrícolas específicas, en particular la aplicación de purines. El mapa de la distribución espacial muestra varias áreas con niveles de Hg más elevados que pueden ser atribuidos a influencias humanas. El delta del Ebro es una de las áreas que refleja los efectos de la actividad humana como consecuencia de la acumulación de metales en la cuenca durante años, así como la cabecera del valle, caracterizada por una intensa actividad minera en el pasado. Otra fuente importante que probablemente incremente el contenido en Hg en suelos del valle del Ebro es la procedente de la deposición atmosférica, debida a las emisiones de las actividades industriales.

Palabras clave adicionales: metales pesados, influencias humanas, capa superior del suelo, distribución espacial, kriging.

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Abbreviations used: AAS (atomic absorption spectrometry), CV (coefficient of variation), Df (degree of freedom), EC (electrical conductivity), FIAS (flow-injection system), OK (ordinary kriging), OM (organic matter), ppb (parts per billion), SD (standard deviation), SOM (soil organic matter).

Introduction

No essential biological function of mercury (Hg) is known. Worldwide Hg concentrations in soils range between 10 and 200 $\mu\text{g kg}^{-1}$ soil (Adriano, 1986; Tack *et al.*, 2005) or according to other studies between 10 $\mu\text{g kg}^{-1}$ and 500 $\mu\text{g kg}^{-1}$ (Alloway, 1995). Although Hg is not abundant in nature (the crustal average of Hg is of the order of 50 $\mu\text{g kg}^{-1}$ or perhaps even lower), it has become widespread as a result of many industrial applications. Commercial production of Hg is made almost entirely from cinnabar (HgS). Hg also occurs in the Earth's crust as complex sulphides with Zn, Fe and other metals, but only to a small extent as native mineral. The most common activities giving rise to emission of Hg are mining and smelting of ores (in particular Cu and Zn smelting), burning of fossil fuels (mainly coal), industrial production processes and consumption-related discharges, including waste incineration. An estimated 10,000 metric tons of Hg are mined each year (Tack *et al.*, 2005). According to Alloway (1995), the annual anthropogenic release of Hg on a global basis was about 3×10^6 kg around the year 1900, and had increased to about three times that amount by the 1970s. Around 45% was emitted to the air, 7% to the water, and 48% to the land.

Mining and other human activities, including combustion of fossil fuels and incineration of waste, and other applications have significantly increased the emission of Hg into the atmosphere. In general, Hg accumulations in soils are associated with atmospheric deposition (Engle *et al.*, 2005). Anthropogenic emission of Hg is about 60-80% of global Hg emission, with about 50% of anthropogenic Hg entering the global cycle (Liu *et al.*, 2003). Many natural and anthropogenic processes intervene in the release of Hg into the atmosphere in form of Hg^0 . This can remain present in the atmosphere between 0.5 and 2 years before it is deposited in the soil (Navarro *et al.*, 1993), which permits transport over large distances. Although Hg released from mining and refining activities undergoes rapid deposition, Lacerda *et al.* (2004) showed that Hg emitted from mining sites to the atmosphere is deposited in the first 40 km from sites. Another source of Hg emissions into the atmosphere is the paper mill. Navarro *et al.* (1993) determined that an important fraction of the Hg emitted by paper mill in Motril (Spain) was deposited locally and decreased with distance from the mill.

The Ebro river zone is intensively industrialized and this human activity is generating a strong impact that

can have negative repercussions on soils, as well as negative effects on the quality of agricultural products. The Ebro basin is an important agriculture area in Spain (44.5% is dedicated to agricultural cultivation and 15% of the basin is grassland) wherein soils on a local scale have been greatly altered by intense agricultural practices. Although Hg uses are now restricted in agricultural uses, regions of intensive agriculture found in alluvial valleys and floodplains are high risk areas to contamination from Hg due to large-scale use of commercial pesticides, in addition to natural accumulations from accumulated sediments, soil weathering, and atmospheric deposition.

Spatial variation can be attributed to inherent geographical properties and geochemical processes (Tao, 1995), whereas temporal variations can be largely attributed to major human perturbations such as industrialization, agricultural practices and urbanization (Li and Wu, 1991; Grabiell *et al.*, 2005). The problems associated with the characterization of heavy metals in the majority of sites are often due to multiple sources of pollution (Boluda *et al.*, 1988; Hanesch *et al.*, 2001; Zarcinas *et al.*, 2004). The purpose of this study was to characterize the Hg topsoil concentrations in quantitative terms and to evaluate the sources of variability in the Ebro basin.

Material and methods

The study area and soil samples

The study area, in the northeast region of the Iberian Peninsula, is framed by three mountain ranges, the Pyrenees to the north, the Iberian Chain to the southwest, and the Catalanian Coastal Ranges to the southeast. Most exposed rocks within the basin area are of the Oligocene-Miocene age (including clastic, evaporite and carbonate facies) and of alluvial and lacustrine origin (Riba *et al.*, 1983; Simon-Gomez, 1989). Contemporaneously, several nested levels of alluvial terraces and sediments developed (Simón and Soriano, 1986). The Ebro river zone, with a population of around 3.25 million, is intensively industrialized. The region of the Ebro river is also an important agricultural area in Spain, with 4.2 million ha (Fig. 1) of agricultural topsoil (the total area of basin is 9.5 million ha).

Soil samples (average 3 kg) were collected between 2003 and 2004 from 624 georeferenced locations. The

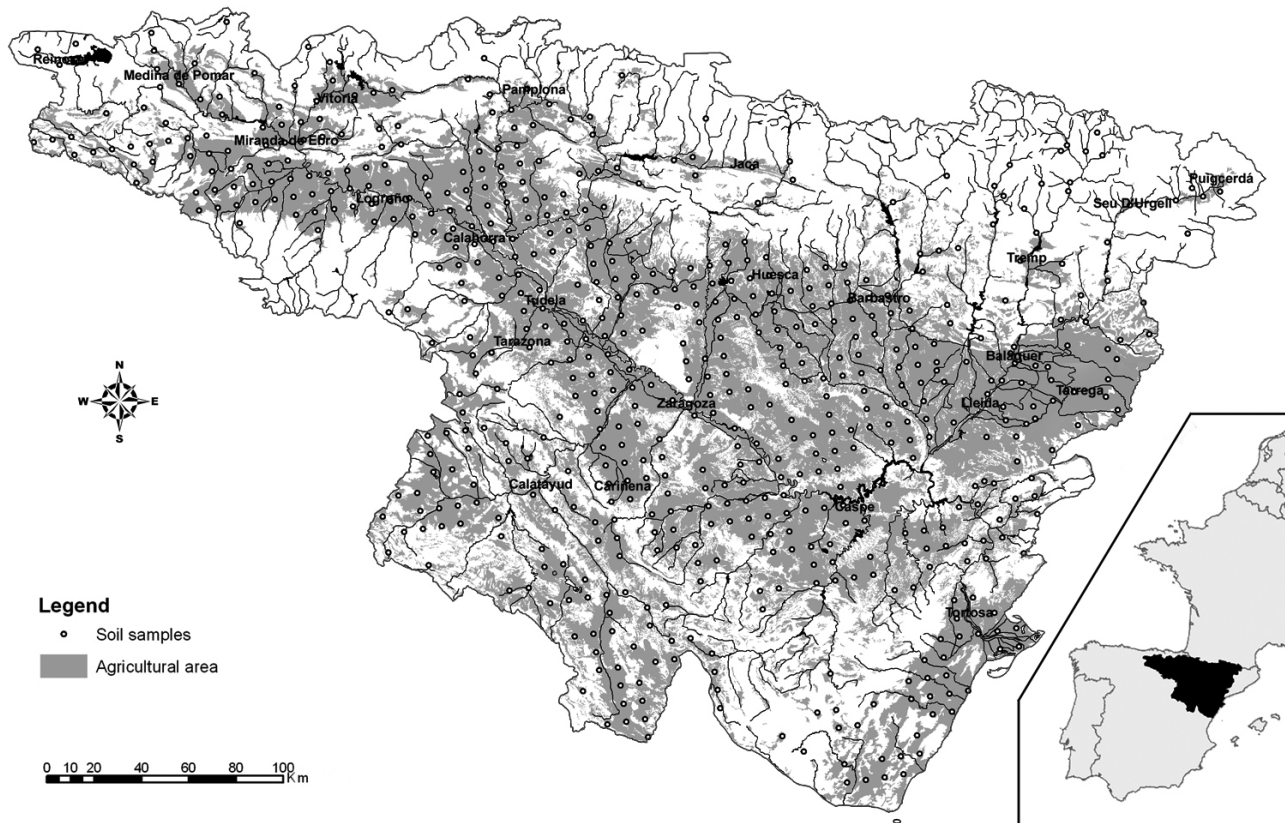


Figure 1. Map of the 624 samples on Ebro basin agricultural area.

basic sampling grid was a square mesh with sampling point at intervals of 8 by 8 km. The samples were defined as composite samples made up of 21 increments collected from the upper 25 cm of soil in a cross pattern, with a 10 m distance between increments (Eijkelkamp soil sampling kit used).

Analytical methods

Soil samples were air-dried, and sieved with a 2 mm grid sieve. After shaking with a dispersing agent, the sand (63 μm -2 mm) was separated from the clay and silt with a 63 μm sieve (wet sieving). The clay (<2 mm) and silt (2-63 μm) fractions were determined by the pipette method (sedimentation). A standard soil analysis was carried out to determine the soil reaction (pH) in a 1:2.5 soil-water suspension (measured by a glass electrode CRISON model Microph 2002) and organic matter (OM, %) by dry combustion (LECO mod. HCN-600) after ignition at 1050°C and discounting the carbon contained in carbonates. Carbonate concentration was

analysed by manometric measurement of CO_2 released following HCl dissolution (Houba *et al.*, 1995) and electrical conductivity (EC) was measured using electrodes.

Hg content was extracted by *aqua regia* digestion (HNO_3 , HCl and H_2O_2) of the soil fraction in microwave (Milestone Ethos 900 plus Mod. 44062) in accordance with the ISO 11466 procedure (International Organization for Standardization, 1995). Hg in soil extracts was determined by cold vapour atomic absorption spectrometry (AAS) in flow-injection system (FIAS); FIAS 100 was used in combination with Perkin Elmer 2100 AAS. Hg vapours were stripped with argon and transferred to the absorption cell. The CV-AAS has been developed to measure low concentrations and FIAS provides excellent selectivity and sensitivity (Bulska *et al.*, 1995; Lalor *et al.*, 2005) showing detection limit of 0.10 ppb. The accuracy of the method was verified through analysis of a calcareous loam soil CRM 141 R standard reference material (Quevauviller *et al.*, 1996).

Statistical and geostatistical analysis

All statistical analysis were carried out using the statistical package SPSS for win V11, GS+ for win V5 and Geostatistical Analyst extension for ArcGis 8.3. In order to stabilise variances in all subsequent statistical analysis, the values of Hg were transformed to their common logarithms. Analysis of variance was used to assess significant differences between different parameters. The confidence interval for Student *t*-test was calculated at $\alpha = 0.05$. These analyses are essential to understanding the relations between soil properties because classical statistical approaches ignore the spatial correlations between sampling points, which include important information (Lin, 2002).

Semivariogram and correlogram were developed to establish the degree of spatial continuity of Hg among data points and establish the range of spatial dependence for soils. The variogram γ is calculated using the relative locations of the samples (Söderström, 1998; Lin, 2002) defined as [1] and correlogram as [2]:

$$\gamma_{(h)} = \frac{1}{2n} \sum_{i=1}^{i=n} [Z(u_i) - Z(u_{i+h})]^2 \quad [1]$$

Where $Z(u_i)$ is the value of Z at location u_i and $Z(u_{i+h})$ is the value of Z at a location separated from u_i by distance h .

$$I_{(h)} = n_{(h)} \frac{\sum_{i=1}^{i=n} \sum_{j=1}^{j=n} [Z(u_i) \times Z(u_j)]}{\sum_{i=1}^{i=n} [Z(u_i)]^2} \quad [2]$$

Where $I_{(h)}$ is the autocorrelation for interval distance class h , $Z(u_i)$ is the value of Z at location u_i and $Z(u_j)$ is the value of Z at a location separated from u_i by distance h .

The spherical model was used to fit the experimental semivariogram. This gives emphasis to reliable estimation of nugget and close-range behaviour, to which interpolation is most sensitive (Yemefack *et al.*, 2005). The spherical (*Sph*) model (Goovaerts, 1998; Oberthür *et al.*, 1999) is defined as:

$$\gamma_{(h)} = Sph\left(\frac{h}{a}\right) = \begin{cases} c_0 + c \left(\frac{3h}{2a} - \frac{1}{2} \left(\frac{h}{a} \right)^3 \right) & \text{if } h \leq a \\ c_0 + c & \text{if } h > a \end{cases} \quad [3]$$

Where $g_{(h)}$ is the semivariance, c_0 is the nugget variance, c is the sill, h is de lag distance and a is the range. The practical range is defined as the distance at which the model value is at 95% of the sill.

The main application of geostatistics to soil science has been the estimation and mapping of soil attributes in unsampled areas. Prediction is made possible by the existence of spatial dependence between observations as assessed by the correlogram or semivariogram. Kriging estimates are calculated as weighted sums of the adjacent sampled concentrations. That is, if data appears to be highly continuous in space, the values nearer to those estimated receive higher weights than those further away (Ersoy *et al.*, 2004). Soil Hg contents were mapped by ordinary kriging (OK). The most likely value $R(u)$ one could expect to encounter in a particular grid cell: using m nearby observations is defined as:

$$R(u) = \sum_{j=1}^{j=m} \lambda_j Z(u_j) \quad [4]$$

Results and discussion

Hg contents, soil properties and correlations

Summary of the statistics of the observations are listed in Table 1. The Hg concentration in this study fell between 1 and 717 $\mu\text{g kg}^{-1}$ (mean 35.6 $\mu\text{g kg}^{-1}$). This is a wide range, although 90% of the values for Hg were estimated between 2.5 and 70 $\mu\text{g kg}^{-1}$. Wu *et al.* (1991) using 4090 samples established Hg levels of 100 $\mu\text{g kg}^{-1}$ for natural or pristine areas and 200 $\mu\text{g kg}^{-1}$ for agricultural and pastoral areas. In general 300 $\mu\text{g kg}^{-1}$ is the threshold value at which toxicity symptoms may occur. In the Ebro basin, this critical value is exceeded in two plots (0.3% of samples) and only five plots higher than 200 $\mu\text{g kg}^{-1}$.

The soil pH ranged from 4.9 to 9 (Table 1). The soil in the area is predominately basic (mean 8.09) and is due to the high percentage of carbonate material present. Mobility and retention is strongly affected by soil pH. Cationic elements tend to be more mobile with decreasing pH. The soil is predominately agricultural and presented low OM content. The average OM content in the investigated area was 2.2% and lay between 0.2% and 13.1%. Organic carbon increases the binding capacity of soil for metals (Boluda, 1988); this effect is probably due to the cation exchange capacity of organic material (Tichy *et al.*, 1997). Di Giulio and Ryan (1987) in North Carolina peatland revealed that the bulk of Hg was associated with OM content. Complexes between Hg and OM are considered to be strong and stable (Liu *et al.*, 2003). The strong bonds that form

Table 1. Statistical summary of Hg concentrations and some soil properties (n=624)

	Mean	SD ¹	Median	Min.	Max.	CV (%) ²	SE ³
Hg, $\mu\text{g kg}^{-1}$	35.60	42.1	27.0	1.0	717.0	118.1	1.68
pH	8.09	0.54	8.2	4.9	9.0	6.7	0.02
SOM, % ⁴	2.20	1.38	1.9	0.2	13.1	62.7	0.05
CaCO ₃ , % ⁵	29.67	16.1	31.0	0.0	79.0	54.2	0.64
EC, dS m ⁻¹ ⁶	0.59	0.85	0.27	0.02	9.18	142	0.03
Sand, %	38.62	17.1	37.9	3.9	96.1	44.3	0.68
Clay, %	21.97	8.7	20.8	1.7	62.3	33.2	0.52
Silt, %	39.36	13.1	39.6	2.0	89.3	39.6	0.35

¹ SD, standard deviation. ² CV, coefficient of variation. ³ SE, standard error. ⁴ SOM, soil organic matter. ⁵ CaCO₃, carbonates. ⁶ EC, soil electrical conductivity.

between Hg and OM create a stable complex of Hg that is considered to be far less bioavailable and mobile than Hg present in the water soluble or iron-exchangeable fractions.

Correlation analysis (Table 2) was carried out to determine the extent of the relationship between soil Hg content and other parameters (the pH, OM, carbonates, EC and particle size). The correlation matrix shows that only EC and silt content do not correlate with the Hg. There is a significant correlation between Hg and OM ($r=0.169$) and between Hg and soil pH ($r=-0.149$) or carbonates ($r=-0.174$) and lower with clay content ($r=0.097$). Contents of Hg tend to be higher in soils with high contents of clay and/or OM (Rodríguez Martín *et al.*, 2006), due to the capacity of clay mineral to absorb cations. Furthermore, humic substances in organic soil can serve as strong reducing and complexing agents and influence the processes controlling mobilization of many toxic metals including Hg. Chen *et al.* (1999) in Florida soil reported that clay content was highly correlated with concentrations of 15 trace elements. These

results were similar to those obtained by Tack *et al.* (2005) in Flanders (Belgium), which showed a significant positive correlation with Hg concentrations but only for organic carbon. Lacerda *et al.* (2004) observed in pasture soils of Southern Amazon high negative correlations ($r=-0.499$) between Hg and soil pH and also demonstrated positive correlations (but not significant) with OM content.

To estimate baseline concentration, the Hg contents will be distributed according to a log-normal distribution (Fig. 2). High data were removed until the skew of the distribution became minimal. The threshold was located at $144 \mu\text{g kg}^{-1}$. Percentile values for Hg are showed in Table 3. These values can be used as reference to determinate a soil might be contaminated or not, anomalous values that presumably were due to anthropogenic inputs (Tobías *et al.*, 1997). The baseline concentration range can be used to assess metal contamination in soil (De Miguel *et al.*, 2002). The term “geochemical baseline concentrations” is often used to express an expected range of element concentrations

Table 2. Pearson correlation matrix for Hg contents and some soil properties

	pH	CaCO ₃	EC	SOM	Silt	Clay
CaCO ₃	0.463***					
EC	-0.054 ^{ns}	0.016 ^{ns}				
SOM	-0.374***	-0.092*	-0.086*			
Silt	-0.092*	-0.239***	-0.265***	-0.202***		
Clay	0.060 ^{ns}	0.056 ^{ns}	-0.064 ^{ns}	0.283***	-0.660***	
Log[Hg]	-0.140***	-0.174***	-0.041 ^{ns}	0.169***	-0.008 ^{ns}	0.097*

Abbreviations, see Table 1. *, **, *** correlation significant at $p<0.05$, $p<0.01$ and $p<0.001$ respectively.

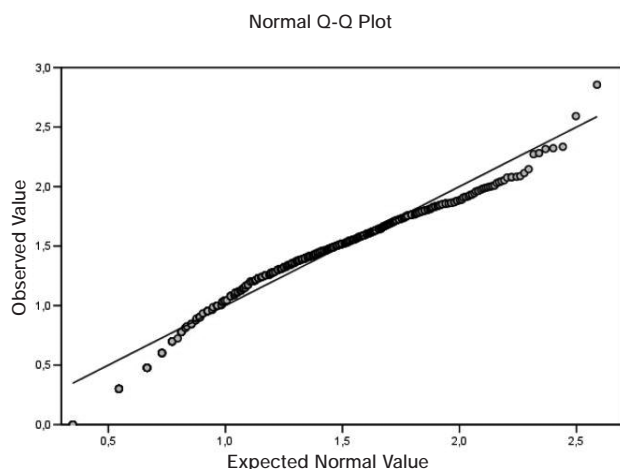


Figure 2. Normal probability plot of mercury contents as $\log[\text{Hg}]$.

around a mean in a normal sample medium but it is not generally a true background concentration (Gil *et al.*, 2004). Soil contamination may be considered when concentration of an element in soil are two to three times greater than the mean background levels (Tobías *et al.*, 1997). Chen *et al.* (1999) recommended the use of baseline concentrations as alternative criteria for assessing possible trace element contamination in soil, or the use of upper limit of the baseline concentration range to assess the background concentration with an acceptable degree of confidence. It was very difficult to compare our results with those reported by other authors. Table 4 shows the range and mean values of Hg contents in topsoil obtained in different studies by various researchers. Most of these studies showed large variability in concentrations depending on the area analysed and on the soil type.

The concentration ranges in the Ebro basin do not in general show high values, the mean value ($35.6 \mu\text{g kg}^{-1}$) is lower than most values reported in literature, and only 21 samples higher than $100 \mu\text{g kg}^{-1}$. Table 5 shows the median and mean values of Hg concentrations in topsoil for crops and lithology. The original Hg sources common to all soils are the minerals constituting the rocks forming the soil parent material. Some investigations (Alloway, 1995) assumed that the levels

of Hg in soil are higher in igneous and sedimentary rock types. Hg accumulated in soils is associated with accumulation of iron and aluminium oxides (Lacerda *et al.*, 2004; Zarcinas *et al.*, 2004). On the other hand the use of fertilisers (commercial fertiliser, manure and sewage sludge), lime and Hg containing fungicides may sometime increase substantially the Hg load in agricultural soils. Cooper and Gillespie (2001) reported that in the 1960s more than 2100 metric tons of Hg was used worldwide per year in agriculture. Sewage sludges disposed on land often contains appreciable amounts of Hg (Li and Wu, 1991; Wu *et al.*, 1991). Multifactor analysis of variance was utilized to determine if lithology and crop factors have a statistically significant effect on topsoil Hg content (Table 6). The results of ANOVA in this study indicate uniform concentration of Hg in Ebro soils. In line with the wide scatter in the data, on some occasions it is difficult to differentiate the effect of each of these factors on the soil. The characterization of heavy metals in the majority of soils is often due to multiple sources (Hanesch *et al.*, 2001; Romic and Romic, 2003).

Geostatistical analysis and Hg mapping

In the geostatistical literature, spatial patterns are usually described in terms of dissimilarity between observations as a function of the separation distance. Experimental semivariogram suggested that the theoretical spherical isotropic model is in reasonable agreement with the data. The theoretical model was plotted in Figure 3. The experimental correlogram (Fig. 4) is referred to as range and is interpreted at the distance beyond which two Hg values can be considered as statistically independent (Oberthür *et al.*, 1999). In our case the correlation becomes negligible at a separation distance of about 80 km. The larger values of the Hg semivariogram at short distances indicate that most of this variability is present over a few kilometres (the highest of variation occurred over distances of <40 km). The nugget effect represents the undetectable experimental error and field variation within the minimum sampling spacing (Guo *et al.*, 2001). The nugget effect

Table 3. Estimate of baseline concentrations for Hg ($\mu\text{g kg}^{-1}$ dry soil) based on the percentile values of 624 data considered

Percentile	5%	25%	50%	75%	90%	95%	99%
Hg ($\mu\text{g kg}^{-1}$)	4.0	15.9	27.0	44.0	68.7	86.0	187.0

Table 4. Some soil Hg contents reported in literature

Site	Range ($\mu\text{g kg}^{-1}$)	Mean ($\mu\text{g kg}^{-1}$)	Reference
Spain	1 - 3729	55.4	Lopez-Arias and Rodríguez (2005)
Madrid (Spain)	5 - 360	32.7	De Miguel <i>et al.</i> (2002)
Belgium	30 - 4190	240	Tack <i>et al.</i> (2005)
Taiwan	16 - 210	55.1	Lin (2002)
Korea	17 - 281	45 - 110	Kim and Kim (1999)
China	20 - 30	65	Li and Wu (1991); Wu <i>et al.</i> (1991)
Illinois (USA)	8 - 123	33	Dreher and Follmer (2004)
Mississippi (USA)	10 - 200	55.1	Cooper and Gillespie (2001)
Florida (USA)	0.6 - 430	12.6	Chen <i>et al.</i> (1999)
Brazilian Amazon	10 - 74	33.8	Lacerda <i>et al.</i> (2004)

($c_0 = 0.087$) suggests that a big variation existed in the small ranges. The sill value ($c = 0.156$) represents total spatial variation (Ersoy *et al.*, 2004) and the range ($a_0 = 36500$) is considered as the distance beyond which observations are not spatially dependent (Gallardo,

2003; Sun *et al.*, 2003). The nugget/sill ratio (56.23%) can be regarded as criterion to classify the spatial dependence of soil properties. If the ratio is <25%, the variable has strong spatial dependence; between 25% and 75%, the variable has moderate spatial dependence;

Table 5. Crops and lithology classification and statistical parameters of Hg concentrations ($\mu\text{g kg}^{-1}$)

	N	Min	1 st Qu ¹	Median	Mean	SD ²	3 rd Qu ¹	Max.	CV (%) ³
<i>Lithology</i>									
Sand wares	18	2.0	21.8	29.5	52.4	60.7	52.0	210.0	115.9
Sandstone	67	5.0	17.0	28.0	34.1	24.5	45.0	122.5	71.9
Limestone	62	1.0	18.0	31.5	39.5	51.4	42.0	391.0	130.1
Armored mud balls	41	3.0	18.0	25.0	33.6	20.5	48.7	77.0	61.0
Quartzites	10	1.0	19.0	35.0	46.8	40.9	70.0	120.0	87.4
Dolostones	8	7.5	19.7	33.0	28.5	11.8	37.0	41.0	41.6
Gravels	145	1.0	17.3	32.0	44.1	66.5	58.0	717.0	150.8
Claystones	95	1.0	13.3	24.4	29.5	22.3	40.4	92.0	75.6
Marls	56	1.0	12.7	25.4	28.5	18.5	42.2	74.0	65.0
Gypsum	46	3.0	15.0	24.5	32.9	27.2	39.0	113.0	82.4
Conglomerates	76	1.0	12.1	22.0	28.4	23.5	35.2	121.0	82.8
<i>Crops</i>									
Cereal	306	1.0	14.0	25.6	33.5	31.7	41.8	216.0	94.7
Citrus	7	26.0	33.0	48.8	56.3	28.7	73.0	111.0	51.0
Fodder farming	91	1.0	15.9	27.1	30.7	21.6	40.0	121.0	70.2
Industrial crops	13	1.0	13.0	25.0	29.2	21.6	37.0	72.2	74.1
Arable land ⁴	30	2.0	16.0	23.5	28.7	20.4	42.0	69.0	71.2
Fruit	44	2.0	13.5	28.5	33.6	25.3	45.9	102.0	75.3
Vegetable garden	9	9.0	14.0	19.0	29.9	22.2	32.0	68.7	74.4
Olive	33	5.0	20.0	33.0	37.4	22.9	58.0	81.0	61.3
Grassland	49	1.0	19.0	36.0	64.8	112.4	60.0	717.0	173.5
Tuber	5	15.0	25.0	27.0	33.1	15.6	46.7	52.0	47.1
Vineyard	37	4.0	17.0	26.0	32.6	25.5	36.6	140.0	78.2
<i>Total</i>	624	1.0	16.0	27.0	35.6	42.1	44.0	717.0	118.1

¹ 1st Qu, 3rd Qu, first and third quartile. ² SD, standard deviation. ³ CV, coefficient of variation. ⁴ Fallow or non-specified cultivation type.

Table 6. Analysis of variance for mercury contents in soils

Source	Sum of squares	Df	Mean square	F-ratio	P-value
Lithology	1.58527	10	0.158527	0.96	0.4788
Crop	2.33003	10	0.233003	1.41	0.1722
Error	99.736	603	0.1654		
Total	103.925	623			

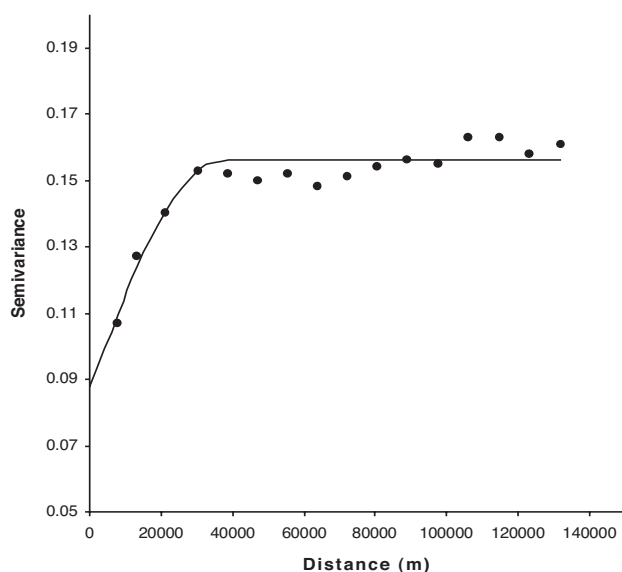
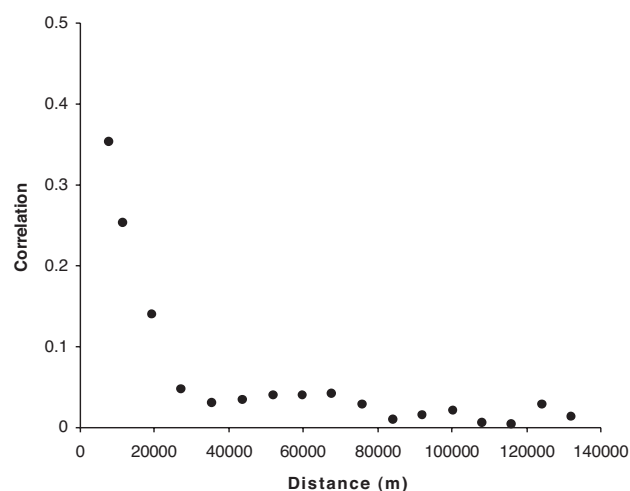
Mercury values were transformed to their common logarithms.

and >75%, the variable shows only weak spatial dependence (Guo *et al.*, 2001; Sun *et al.*, 2003; Liu *et al.*, 2004). Usually, strong spatial dependence of soil properties can be attributed to intrinsic properties, and weak spatial dependence can be attributed to extrinsic aspects (Liu *et al.*, 2004; Rodríguez Martín *et al.*, 2006). A value was interpolated with OK based on spherical semivariogram. The kriging contour map of Hg (Fig. 5) indicated that there were three areas of high concentration levels.

Evidence of human influence can be seen surrounding the Ebro delta, containing 4 of the 6 samples that exceeded the threshold of 200 $\mu\text{g kg}^{-1}$. The delta is the largest wetland of Catalonia and second largest of Spain, with more than 20,000 ha of rice paddy. Hg hotspots in the Ebro delta are associated with the deposition of large quantities of silt and clay sized particles. In addition, during flooding, the higher energy flows were capable of transporting bulk sediments of industrial and agricultural land in the Ebro river to the delta. High Hg

concentrations would be produced by physical partitioning (and concentration) of fine-grained sediment into discrete depositional units. The capability of sediments to record anthropogenic influences is well known (Boluđa *et al.*, 1993; Birch *et al.*, 2001; Romić and Romić, 2003). Hg concentrations in sediment tended to be higher in estuaries (Di Giulio and Ryan, 1987). Miller *et al.* (2003) in Essequibo and Mazaruni river basins (Guyana) suggest that much of the Hg found in the alluvial deposits was related to anthropogenic sources, including mining activities along the river.

Another area with high concentration levels was found on the Ebro headwaters. The highest value of Hg (717 $\mu\text{g kg}^{-1}$) was found near Reinosá. The head of the Ebro valley is located within the province of Santander. Throughout history, mining has been of great importance in this area. Mines such as Llorada (Lois) have been exploited since Roman times to extract cinnabar. In Asturias, the towns of Pola de Lena, Mieres, Langreo, Villaviciosa and Caravias are areas characterized by the

**Figure 3.** Semivariogram for Hg topsoil values.**Figure 4.** Correlogram for Hg topsoil values.

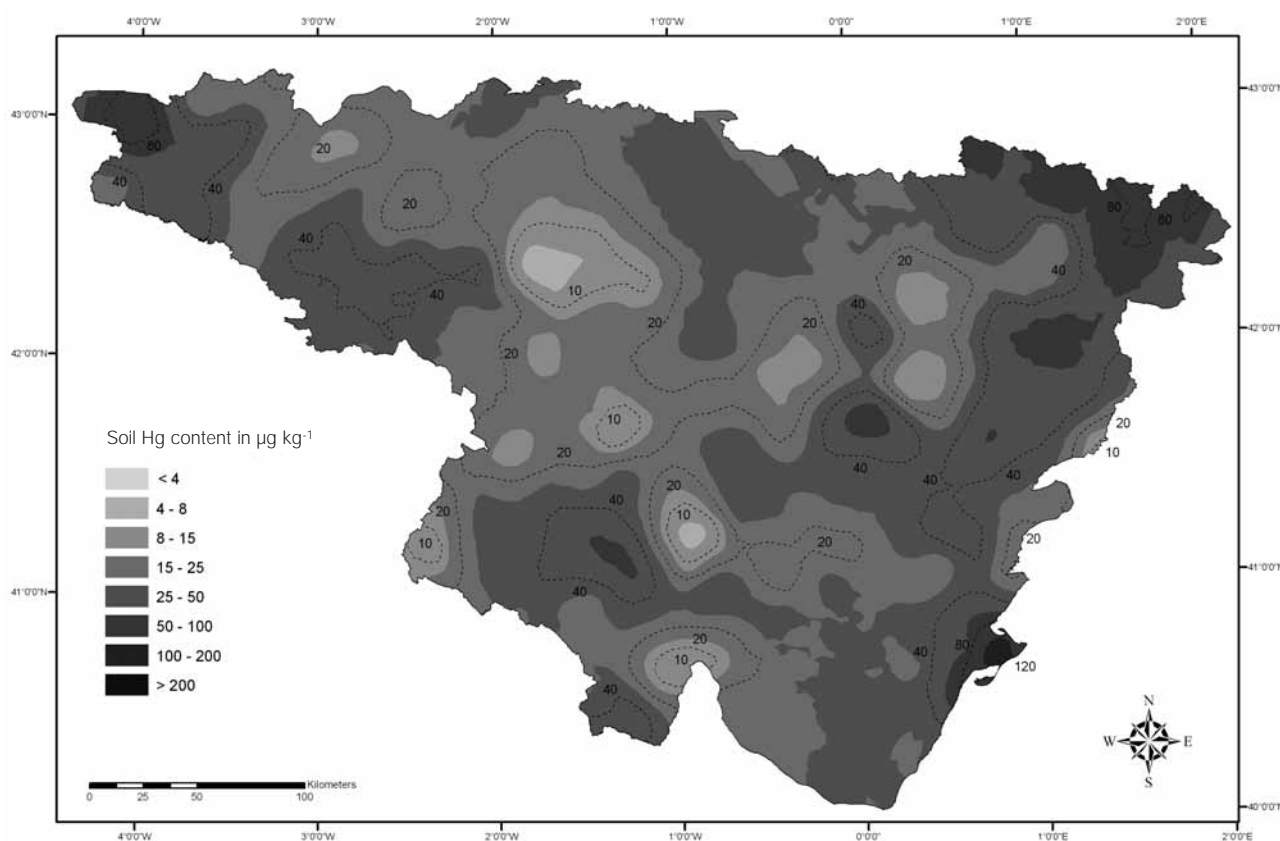


Figure 5. Kriging contour map of Hg contents in agricultural topsoils from Ebro Valley.

presence of important HgS deposits, and by intense Hg mining and smelting activities in the past. The influence of cinnabar deposits on the Hg levels in soils has been studied by John *et al.* (1975), in which was found the highest Hg concentrations ($0.75 - 2.32 \mu\text{g g}^{-1}$) in British Columbia soils near the Pinchi Hg mine. Martinez-Cortizas *et al.* (1999) correlated Hg concentrations in Galicia peat bog with the history of Hg mining and metallurgy in Spain. The first antropogenic componet of acumulation corresponded to the Roman Empire, when the cinnabar refining was introduced in Spain. Barghigiani and Ristori (1994) in Amiata (Italy) found even higher soil Hg concentrations ($8.9 - 27.9 \mu\text{g g}^{-1}$) and related the Hg contamination of agricultural products due to mining activity. Other reports (Richard *et al.*, 2000; Miller *et al.*, 2003) indicated enriched Hg concentrations occurred in soils near cinnabar and basemetal ore deposits. Other direct inputs of Hg associated with the study area are the gold mining of Figueras, Valledor, Bagega y Narcea. The majority of these gold mining operations utilize Hg amalgamation methods in the recovery process. Hg amalgamation was used by the

phoenicians and the carthagians to recover gold and silver from ore bodies more than 4500 year ago and the basic process has changed little since its inception. Nonetheless, it is generally accepted that most of the Hg emitted during roasting of the amalgam is rapidly deposited close to mining sites (Miller *et al.*, 2003). This area (the Ebro headwaters) was polluted by Hg from dry and wet deposition of atmosphere due to mining and smelting activities.

Other high values were also located in the north-east of the Ebro valley, primarily on grassland areas. A possible explanation of the markedly increased Hg levels in this investigated part of valley can be found in the presence of higher OM content. The grassland samples in this region of the Ebro River were predominantly in mountainous regions, at higher altitudes, and contained high percentages of OM. Some of these samples were collected on peat bog. Hg content in the peat bog was higher (Martinez-Cortizas *et al.*, 1999). There are high affinity and adsorption capacity of peat for Hg. Arfstrom *et al.* (2000) in Everglades peat soils (Florida, USA) found ranges from 117 to $300 \mu\text{g g}^{-1}$ (mean 209

$\mu\text{g g}^{-1}$) and assumed that a significant portion of the increased Hg content came from the deposition of anthropogenic atmospheric Hg. Grigal *et al.* (2000) evaluating the Hg budget in Minnesota (USA) showed that a significant fraction of Hg annually deposited on uplands may return to the atmosphere but in peatland the annual inputs of Hg were much greater than outputs. Hg in peat is condensed following the decomposition of OM and peatland can be considered as areas of Hg drainage (Di Giulio and Ryan, 1987).

The possible anthropogenic input of Hg to lands (Dreher and Follmer, 2004) include emissions from coal-burning power plants and industrial boilers, municipal waste incinerators, phosphate-rock fertilizers, cement and lime kilns, petroleum refineries, landfills, animal manures and sewage sludge. The atmosphere contains ≈ 850 metric tons of Hg, about 95% as Hg^0 vapour and the remaining 5% associated with particulates and organomercury compounds (Arfstrom *et al.*, 2000). Hg vapour resides for 0.5-2 years in the atmosphere, and may travel far from its sources. Particulate Hg associated with ash and soot may be efficiently removed by precipitation and deposited relatively close to the source. Dreher and Follmer (2004) estimated that 70-80% of Hg currently emitted to the atmosphere is of anthropogenic origin. Anthropogenic Hg emissions have increased with the industrialization of modern societies over the past 100 to 150 yr (Martinez-Cortizas *et al.*, 1999). Since 1900, anthropogenic emissions increased largely due to combustion of fossil fuel and burning of industrial and municipal waste. A significant portion of the increased Hg content in the north-east of the Ebro valley probably come from the deposition of anthropogenic atmospheric Hg, but the specific sources of Hg cannot be determined on the basis of data collected in this research. Many industrial and municipalities solid waste incinerators operate in the Ebro valley.

Other sources of anthropic Hg input on grassland or cultivation lands in the Ebro basin can be caused by the introduction of metal supplementation from organic fertilisation (principally pig slurries) on a local scale. This practice is so universal in the north-east of the Ebro valley (Rodríguez Martín *et al.*, 2006) that the high Hg concentrations found in this area are presumably caused by this practice. Dreher and Follmer (2004) showed that sewage sludge were an important local sources of Hg.

As synthesis, the Hg content in the agricultural soils tested demonstrated normal concentrations, in spite of the anthropic activity in the area.

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