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Source Identification of Soil Mercury in the Spanish Islands

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Abstract This study spatially analysed the relation between mercury (Hg) content in soil and Hg in rock fragment for the purpose of assessing natural soil Hg contribution compared with Hg from human inputs. We present the Hg content of 318 soil and rock fragment samples from 11 islands distributed into two Spanish archipelagos (the volcanic Canary Islands [Canaries] and the Mediterranean Balearic [Balearic] islands). Assumedly both are located far enough away from continental Hg sources to be able to minimise the effects of diffuse pollution. Physical and chemical soil properties were also specified for the samples. Hg contents were significantly greater in the Balearic limestone soils (61 μg kg^{-1}) than in the volcanic soils of the Canaries (33 μg kg^{-1}). Hg levels were also greater in topsoil than in rocky fragments, especially on the Balearics. The soil-to-rock ratios varied between 1 and 30. Interestingly, the highest topsoil-to-rock Hg ratio (>16 ×) was found in the vicinity of a coal-fired power plant in Majorca, whereas no similar areas in the Canary archipelago were identified.

Mercury (Hg) is a toxic element that is naturally present in the environment at very low concentrations (Göthberg and Greger 2006). Its concentration in soil ranges between 10 and 200 μg kg^{-1} (Adriano 2001; Tack et al. 2005); however, at times, it may reach 500 μg kg^{-1} (Adriano 2001). Hg contents in nature <50 μg kg^{-1} are considered normal. Nonetheless, despite its low concentration, Hg is seen as one of the most toxic elements for the majority of living organisms and is considered by the United Nation's International Chemical Safety Program to be one of the six worst pollutants on our planet. Its known toxicity is conveyed from its bioaccumulation capacity and moves upward through the food web (Krabbenhoft et al. 2007). Critical limits for Hg are expressed as added metal content of soil if it is >130 μg kg^{-1} (Tipping et al. 2010). The most relevant effects of Hg in most taxonomic groups are adverse effects on reproduction, immune response, and neurological impairment, as well as damage to the central nervous system, liver, and kidney (Dietz et al. 2000).

Hg concentration in soil and its distribution depend mainly on the composition of the original material (Bueno et al. 2009), its properties, and the edaphogenetic processes intervening in its formation. Moreover, accumulation of Hg in soil may be associated with the accumulation of iron and aluminium oxides (Wang et al. 2011; Zarcinas et al. 2004). Likewise, certain parameters, such as the type and content of clays (Chen et al. 1999), pH (Rodríguez Martín et al. 2009b; Lacerda et al. 2004) or organic matter (Gil et al. 2010; Pant and Allen 2007), play a key role in the retention and accumulation of Hg in soil.

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Hg atmospheric inputs increase Hg content in soils (Engle et al. 2005). Natural Hg sources, such as volcanic eruptions and emissions from oceans, contribute approximately one-third of current worldwide Hg air emissions (Pyle and Mather 2003), whereas anthropogenic emissions account for the remaining two-thirds (Nriagu 1989; Schuster et al. 2002). Approximately half of the anthropogenic sources of Hg come from re-emissions. Industrial activity, mining, burning of fossil fuels, and waste incineration all increase Hg emissions into the atmosphere (Aelion et al. 2009; Liu et al. 2003; Lacerda et al. 2004). Of these pollution sources, coal-fired power stations are the most important individual Hg source. In the United States, 49 tons of Hg are emitted directly into the air every year (Coequyt et al. 1999). Spain is the fourth country in Europe as far as Hg emissions are concerned at 23 t/year emitted (Pacyna et al. 2006) (behind Germany, which emits (23.4 t/year), and most of these emissions come from coal-fired fuel (Pacyna et al. 2006). Emitted Hg can remain in the atmosphere for 0.5–2 years before being deposited on soil (Schroeder and Munthe 1998), which enables it to be transported over long distances from its emission sources.

The main problem lies in distinguishing human input (pollution) from natural Hg input. Hg emitted through industrial activity does not present any sign of its anthropogenic origin, and determining which part of the Hg content in soil is of a natural origin (or not) normally proves to be a complex issue. This study focuses on two archipelagos with completely different geographic formations: the Balearic Islands (also known as the Balearics) with limestone lithologies, and the Canary Islands (also known as the Canaries) of volcanic origin. Both insular complexes are considerably isolated from the continent, thus avoiding, in principle, diffuse pollution sources or those of difficult interpretation. Our study aimed to: (1) assess Hg contents in the soils of these islands by determining the levels of Hg in soil and on rocks according to different lithologies; (2) study the analogy between soil values and the corresponding rocks in relation to the main edaphic parameters associated with their dynamics and retention; (3) generate maps with continuous surfaces to show the spatial variability of Hg in both soil and subsoil; and (4) detect pollution or Hg input sources insofar as far as possible.

Materials and Methods

Study Area and Sampling

The Canaries are an archipelago formed by seven islands of volcanic origin that are new in geological terms: They were formed barely 30 million years ago. They are located southwest of Spain in the Atlantic Ocean (Fig. 1) near the Tropic of Cancer and the western Moroccan coastline (between coordinates 27°37′ and 29°25′ northern latitude and 13°20′ and 18°10′ western longitude). Their climate is subtropical but may vary locally according to altitude and northern or southern slope. Variability in climate brings about broad biological diversity as well as landscape and geological wealth, which justify the 146 protected natural areas with 3,014 km^2 (41 % from the total surface of archipelago) as well as the fact that some isles are UNESCO biosphere reserves.

The Balearics are formed by four islands located in the east Iberian Peninsula and to the extreme west of the Mediterranean Sea (Fig. 1). They are formed mainly by calcareous lithologies, which are marine in origin, and they make up the part emerging from the extension heading northeast of the Baetic mountain system formed during the Tertiary. As a whole, the climate is purely Mediterranean, with annual rainfall of 350–650 mm. The entire archipelago surface covers 5013 km^2, of which 1,874 km^2 (37 %) correspond to protected areas (total of 86 protected areas).

The basic sampling grid was square mesh with sampling points at intervals of 8 × 8 km. Based on a selection of plots of agricultural/pastoral land use, samples were located using orthophotos (1 m/pixel) and topographics maps on a scale of 1:25,000 after omitting those plots whose land use was of a forest type. A systematic grid yielded 59 sampling plots on the Canaries archipelago and 41 on the Balearics archipelago. Sampling points were located by way of global positioning system. At each sampling site, 21 subsamples were taken with the Eijkelkamp soil sampling kit from the upper 25 cm of soil to obtain three soil subsamples from each location. Subsamples were thoroughly mixed in the field to select 1 kg soil. Each sample was air-dried and then sieved to obtain a sample with rocky fragments of >6 mm to determine Hg contents in rocks, and another fine soil sample, below 2 mm, to determine Hg in topsoil and to analyse the edaphic parameters of interest in 318 soil samples.

Analytical Methods

Soil samples were taken to the laboratory to be air-dried and sieved with a 2-mm grid sieve. Each sample's soil texture was determined. After shaking with a dispersing agent, sand (63 μm to 2 mm) was separated from clay and silt with a 63-μm sieve (wet sieving). Clay (<2 μm) and silt (2- to 63-μm) fractions were determined by pipette method (sedimentation). Standard soil analysis was performed to determine first the soil reaction (pH) in a 1:2.5 soil and water suspension (measured by a glass electrode CRISON model Microph 2002). Soil organic matter (SOM) was analysed by the Walkley–Black method (Walkley 1935)

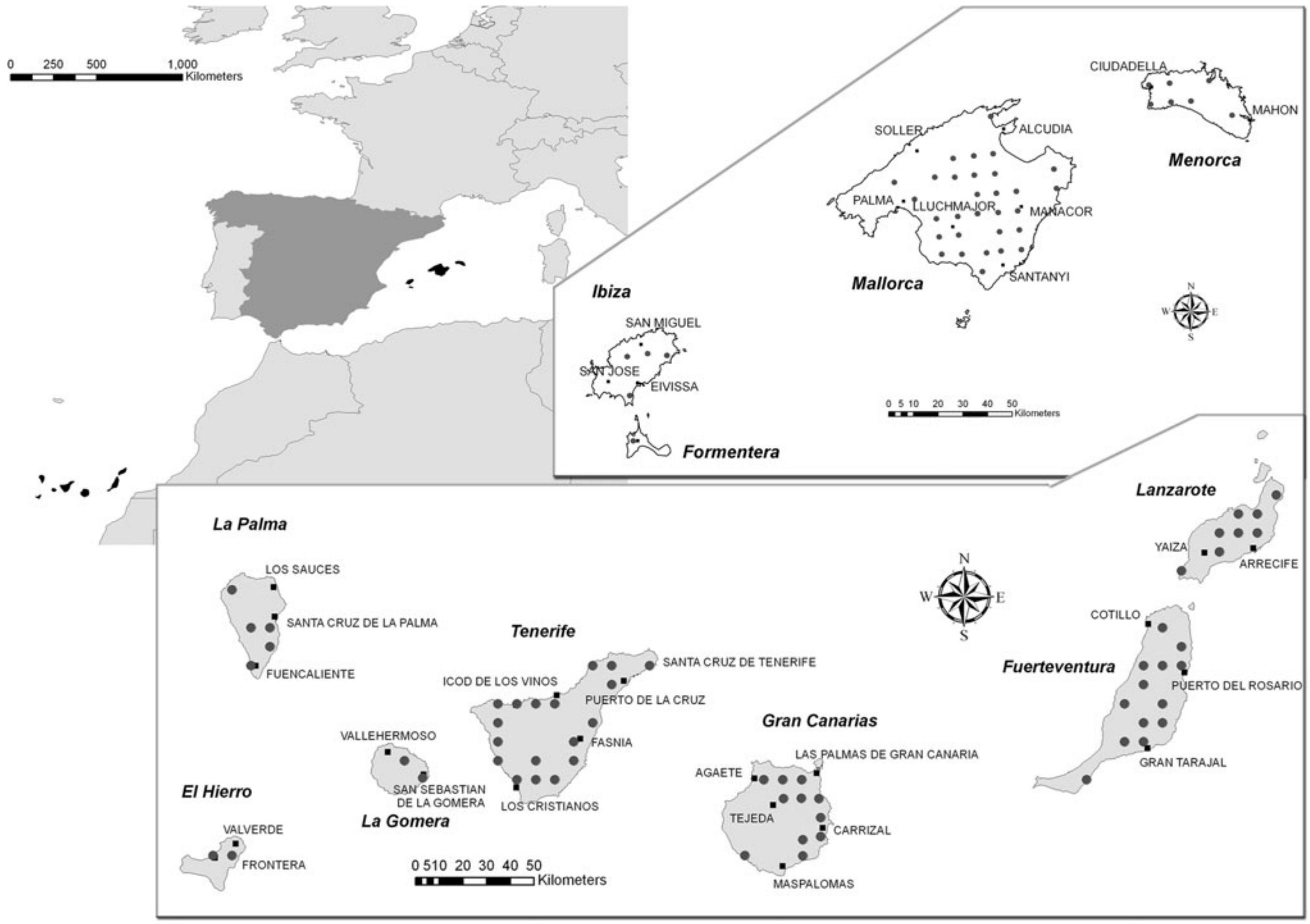

Fig. 1 Localization of Spanish islands and soil samples

and, secondly, organic carbon by dry combustion (LECO mod. HCN-600) after ignition at 1,050 °C and by discounting the carbon contained in carbonates. Carbonate concentration was analysed by a manometric measurement of carbon dioxide (CO_2) released after acid (HCl) dissolution. In addition, exchangeable K and available phosphorous were determined using Olsen's extraction method.

Total Hg (THg) analyses were performed using a direct Hg analyzer (DMA80 [an atomic absorption spectrophotometer]; Milestone, Wesleyan University, Middletown, CT). The results of this detection system were previously validated for solid and liquid matrices (United States Environmental Protection Agency 7473). The limits of detection and quantification were 0.24 and 0.6 μg kg^{-1}, respectively. Method validation of the analytical procedure was performed with a calcareous loam soil (BCR-141 R), obtained from the European Commission Community Bureau of Reference, with 0.24 ± 0.03 mg kg^{-1} of total Hg. All of the materials used for the Hg analysis in this study were acid-washed with 10 % HNO_3 and carefully rinsed with ultrapure water (Milli-Q system; Millipore, Bedford, MA).

Statistical and Geostatistical Analyses

Basic statistical analyses (mean, quartile, SD, correlations, and analysis of variance) were performed to understand the relations among different soil parameters, Hg, and soil lithology. The confidence interval for the Student t test was calculated at $\alpha = 0.05$. In addition, we used geostatistics to assess the spatial variation of the studied attributes (Goovaerts 1997). Semivariograms were used to establish the degree of spatial continuity of Hg among data points and establish the range of spatial dependence for soils. The variogram (γ) was calculated using the relative locations of the samples defined as follows:

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

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.

The spherical model was used to fit the experimental semivariogram as follows:

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

where $\gamma_{(h)}$ is the semivariance, C_0 is the nugget variance, C is the sill, h is the 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.

Kriging estimates were calculated as weighted sums of the adjacent sampled concentrations. Soil and rocky Hg contents were mapped by ordinary kriging (OK). The most likely value $R(u)$ one could expect to encounter in a particular grid cell when using m nearby observations was defined as follows:

$$R(u) = \sum_{j=1}^{j=m} \lambda_j Z(u_i) \quad (3)$$

A geostatistical analyst extension for ArcGis 9.2 was used to generate grids with Hg values and topsoil/rock ratios to assess increased Hg in soil. The resulting estimations were determined by means of cross-validation in ArcGis (Holy et al. 2009).

Results and Discussion

Soil Properties and Hg Contents

The Hg concentration was in the range of 1–349 µg kg^{-1} (mean 47.4). This is a wide-ranging variation, although 90 % of the values for Hg are estimated to be between 2 and 63 µg kg^{-1}. In Europe, Hg content in topsoil is 22 µg kg^{-1} (ranging 5–1,350 [Salminen et al. 2005]). Wu et al. (1991) used 4,090 samples and established Hg levels of 100 µg kg^{-1} for natural or pristine areas and 200 µg kg^{-1} for agricultural and pastoral areas. By and large, 300 µg kg is the threshold value at which toxicity symptoms may occur. In Mediterranean soils, Gil et al. (2010) established a reference value for Hg of 25 µg kg^{-1} and detected that 40 % of soils exceed this concentration. In the present study, this critical value (300 µg kg^{-1}) is exceeded in two plots.

Table 1 lists the average soil Hg values obtained for different lithologies in terms of how the original material influences Hg content in soil. Although this study found no statistically significant differences indicating a direct influence of Hg content on soil, the general trend is that Hg concentrations are greater in soils with sedimentary lithologies than in igneous lithological soils. Nevertheless, some works (Alloway 1995) assume that the levels of Hg in soils are greater than in igneous lithologies and some sedimentary rock types. In sedimentary rocks, formed by the compactation and compression of rocky fragments and by primary or secondary minerals, such as clays or chemical precipitates, e.g., $CaCO_3$, the quantity of this trace element depends on the properties of the sedimented material, the matrix, and the concentrations of metals in water when sediments are deposited. The chemical composition of parent material and weathering processes naturally affects the concentration of the different heavy metals in soils (Gimeno-García et al. 1995; Lacerda et al. 2004; Zarcinas et al. 2004). However, and according to the results obtained, it appears that certain edaphic parameters (SOM pH, granulometric fractions, etc.) present a greater natural influence in this sense.

Table 1 Soil mean Hg concentrations (µg kg^{-1}) in accordance with the described lithological classes

Lithology	No. of samples	Hg
Consolidated-clastic rocks (conglomerate and sandstone)	6	13.04
Calcareous rocks (limestones)	111	10.77
Igneous rocks (volcanic rocks)	177	9.14
Metamorphic rocks (slate and marble)	12	7.80
Eolian sands	6	8.13

Summary statistics of soils parameters and Hg contents in topsoils are listed in Table 2. The mean percentage of organic matter found in the analysed samples is 3.12 %, and there are no significant differences between the soils from the two archipelagos. Organic C in soil increases the binding capacity for metals (Boluda 1988). Soil pH ranges from 4.3 to 9.5, with a mean value of 8.1 (Table 1), and the pH values recorded on the Canaries are more acidic. The Balearic Islands soil is predominately basic (mean 8.3), which is due to the high percentage of carbonate material present. Mobility and retention of heavy metals are also strongly affected by soil pH; for instance, the lower the pH, the more mobile cationic elements tend to be. The clay fraction percentages are greater for the Balearics (26 %) than in the soils on the Canaries, which are of volcanic origin (13 %). Soil granulometric fractions are also related with the content of metals in soil, particularly clay contents, which tend to retain metals (Chen et al. 1999; Tack et al. 2005).

Correlation analysis (Table 2) shows a significant association between Hg and SOM ($r = 0.59$) and between Hg and clay content ($r = 0.49$) or soil pH ($r = -0.45$). Hg contents tend to be greater in soils with high clay and/or SOM contents (Rodríguez Martín et al. 2009a). The complexes between SOM and Hg are considered strong and stable (Liu et al. 2003). Hg usually tends to accumulate in the finest soil particles because of the increases in specific area (Bueno et al. 2009), and, in general, clays present negative charges and tend to undertaken sorption of

Table 2 Statistical summary of soil parameters and Hg concentration (μg kg^{-1})

Parameters	Mean	Median	SD	First quartile	Third quartile	Hg correlation
SOM	3.12	2.76	2.20	1.81	3.76	0.59 ***
Soil pH	8.1	8.2	0.90	7.8	8.5	−0.45 ***
EC	0.61	0.27	1.41	0.22	0.39	−0.06 NS
$CaCO_3$	19.3	13.0	21.3	3	28	−0.01 NS
P_2O_5	936	576	1,028	418	1,157	−0.09 NS
K_2O	34.9	21.0	39.2	9	42	0.32 **
Sand	44.7	41	20.5	29	60	−0.36 ***
Silt	35.3	36	12.7	25	46	0.26 **
Clay	19.3	20	11.5	9	27	0.49 ***
Soil Hg	47.4	31.5	54.1	17	52	

$CaCO_3$ carbonates (%), *EC* soil electrical conductivity (dS m^{-1})

cations, and they are associated with Hg retention in soil. Chen et al. (1999) reported that soils with highly clay content were correlated with concentrations of 15 trace elements. These results are similar to those obtained by Tack et al. (2005), who found a significant positive correlation with Hg concentrations but only for organic C. Our results showed a negatively significant correlation between Hg and pH ($r = -0.45$), and similar values were also recorded by Lacerda et al. (2004) in pasture soils ($r = -0.499$), which also showed positive, but not significant, correlations with SOM content.

The Hg contents statistics in the two archipelagos are listed in Table 3. The Hg topsoil concentration in this study ranges from 12 to 350 μg kg^{-1} (mean 61.1 μg kg^{-1}) on the Balearics and 3 and 159 μg kg^{-1} (mean 33.2 μg kg^{-1}) on the Canaries. In addition to presenting different lithologies, Hg content in rock (Table 3) is similar for the Canaries (mean 9.1 μg kg^{-1}) and the Balearics (mean 11.1 μg kg^{-1}). The concentration ranges in rocky fragments do not show high values. In general, Hg contents tend to be greater in soils than in rocks. In addition, the variability of Hg in soil is associated with the variability of soil's physicochemical properties. Organic matter, pH, clay minerals, metal oxides, oxidation–reduction reactions, ionic exchange processes, or adsorption, desorption, and complexation phenomena are the main edaphic characteristics relating to retention of metals in soil.

Furthermore, anthropogenic inputs have also greatly contributed to increase Hg content in soil irrespective of either the physicochemical properties or the influence of the parent material. Several productive activities, such as mining, smelting, industry, power production, pesticides production, or waste treatment and spillage, have been identified as sources of Hg into the environment (Aelion et al. 2009; Christoforidis and Stamatis 2009; García-Sánchez et al. 2009; Gbor et al. 2007; Bueno et al. 2009). Emissions from stacks of coal-fired power plants, for instance, include fly ash, which escapes particulate-retention devices and pollutants emitted in the volatile phase (López Alonso et al. 2003; Goodarzi 2009; Weir et al. 2010). All of these Hg inputs are deposited on the surface and end up entering soil. In this way, Hg contents in soil increase compared with the input deriving from the weathering of constituent rocks.

Geostatistics Analysis and Spatial Relations

Experimental semivariograms and variogram models are presented in Fig. 2. The range of spatial correlation is significantly greater on the Balearics than on the Canaries. In addition, the variogram range is consistently greater for Hg in topsoil than for Hg in rock fragments. The range of spatial correlation should be interpreted as the separation distance beyond which observations are not spatially

Table 3 Statistical summary of Hg concentrations (in μg kg^{-1}) in topsoil and rocks from soil of the Balearics and Canaries

Topsoil/rock	No. of samples	Mean	Median	SD	First quartile	Third quartile	P 90	P 95	P 99
Topsoil									
Balearics	125	61.1	39.09	63.51	28.29	59.33	116.9	225.2	327.9
Canaries	193	33.2	20.39	32.94	12.13	42.78	82.72	95.56	158.9
Rock									
Balearics	129	11.1	5.65	14.43	3.74	12.06	22.56	43.93	82.6
Canaries	188	9.12	6.58	8.03	4.35	11.63	16.12	20.74	46.94

P90, P95, and P99 = P90, P95 and P99 percentiles, respectively

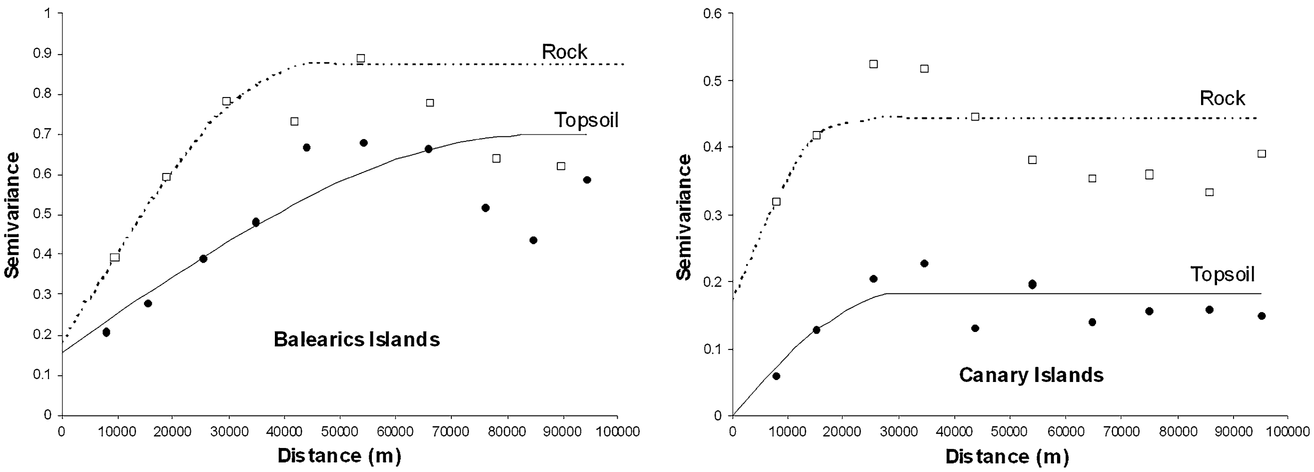

Fig. 2 Semivariogram for the topsoil and rock Hg contents in the Balearics and Canaries

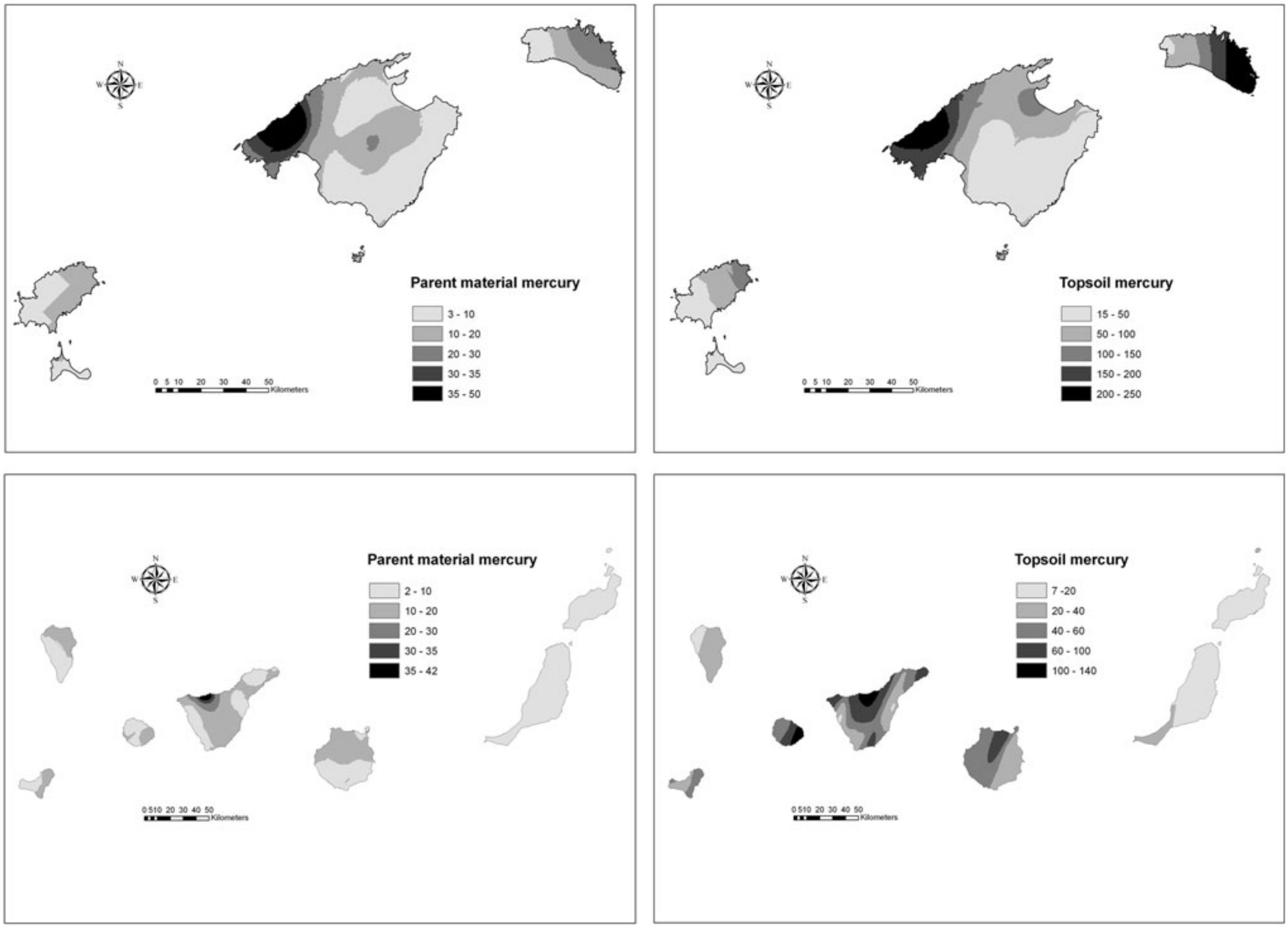

Fig. 3 Kriging maps of the Hg content (μg kg^{-1}) in topsoil and parent material in the Balearics and Canaries

dependent (Sun et al. 2003). The spatial structure of Hg is determined by soil-forming factors (mainly parent materials) and anthropogenic activities (agricultural practices and industry). In contrast, the spatial variation in the Hg content of rocky fragments can be attributed uniquely to inherent geochemical processes that correspond to both mineralogical structures and bedrock influence (Rodríguez Martín et al. 2007).

The differences noted between the two archipelagos may be attributed to the different geological process that took place on each one. Furthermore, according to the semivariograms (Fig. 2), the highest range values were found for Hg in soil (notably greater on the Balearics [approximate range of 84 km]). This may possibly be the result of greater pollution of an atmospheric-deposition type. At any rate, the variability imputable to the lithological component represents the smallest ranges when adjusting the variogram on both archipelagos (45 km on the Balearics and approximately 20 km on the Canaries).

Figure 3 shows the kriging contour map of soil and rocky fragments on both the Balearics and the Canaries. A value is interpolated with ordinary kriging based on a spherical semivariogram and neighbouring points within the range of influence for each factor semivariogram. Maps of the rock Hg contents represent variability of either the natural component or the lithological domain, which in turn reflects variations at shorter distances than the soil Hg maps, where relations with edaphic variables, such as SOM or clays, among others, favour natural Hg accumulation. In principle, the lithological influence in soil contents is obvious. In general terms, the areas with more Hg accumulation in soil are associated with those areas whose values in rock are greater. This becomes particularly evident in northeastern areas of the Island of Majorca (Balearics) or northwards of the Island of Tenerife (Canaries). Nonetheless, it is known that some Hg in soil is associated with an anthropic influence (Aelion et al. 2009; Carbonell et al. 2011; Cooper and Gillespie 2001; Rodríguez Martín et al. 2009a), particularly in areas with mining activities where extremely high concentrations are reached (Bueno et al. 2009).

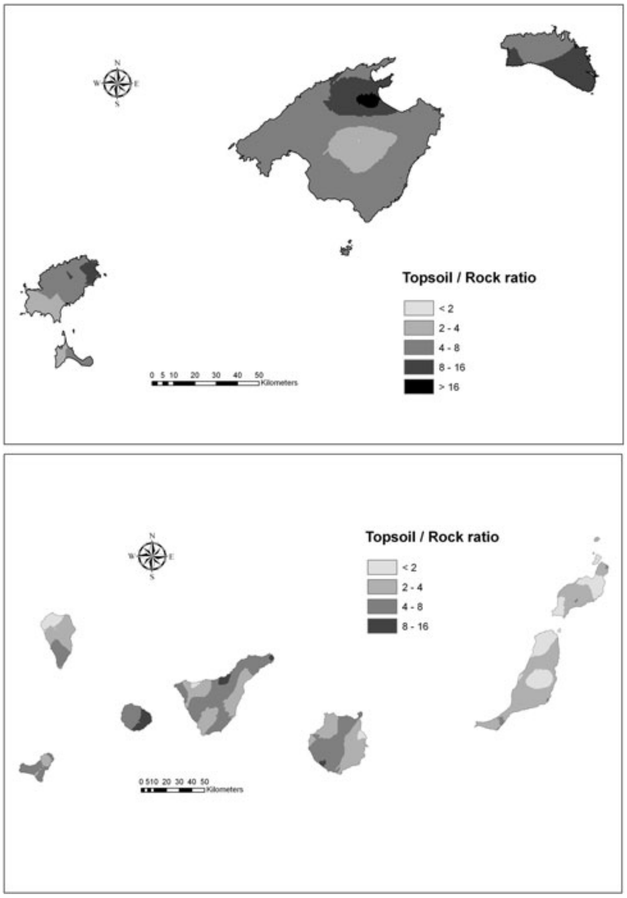

Fig. 4 Map showing topsoil-to-rock Hg ratios

Kriging maps of the topsoil/rock Hg content ratio (Fig. 4) have been used to identify areas that may suggest pollution inputs by means of high ratios. Soil metal contamination may be considered when the metal concentration in soil is 8 times greater than the litogenic content (the real geochemical baseline). These levels were greater on the Majorca Island, where there are areas whose lithogenic content is 16 times greater (Fig. 4). In Majorca, greater ratio values (Fig. 4) are found near a coal-fired power plant (with a capacity to generate 218 MW). Coal-burning power plants are an important source of Hg emissions (Furl and Meredith 2011; Wang et al. 2010; Yang and Wang 2008). The "Mercury Falling" study (Coequyt et al. 1999), which is based on >1,200 power plants dotted around the United States, estimated that 49 tons of Hg are emitted directly to the atmosphere every year. In Europe, coal-firing power plants are the most important individual Hg pollution sources (Pacyna et al. 2006). Coal combustion in electric power plants alone contributes >26 % to the total Hg emissions in Europe (236 tons/year). In Spain, they account for 47 % of the total Hg emissions from all coal-fired power plants (López Alonso et al. 2003). The presence and accumulation of Hg in soil around power plants are more significant in the vicinity of those power plants with a large power production capacity, which is the case of As Pontes in Galicia (northeast Spain) at 1,400 MW (Nóvoa-Muñoz et al. 2008).

The present study shows that this power station (as a local source) is significantly associated with increased Hg accumulation in soil (by atmospheric deposition). Nonetheless, its influence on Hg content in soils rapidly decreases with distance, implying we can assume that certain edaphic parameters (SOM, clays, and high pH) facilitate the immobilisation of a large part of Hg in these soils. Nevertheless, this Hg could pose a greater risk for the S'Albufera wetland (1,700 ha; declared a natural reserve in 1988), which borders this power plant to the north, where some 3,000 fauna and flora species live.

Conclusion

Hg content in soils on Spanish islands does not contribute to excessively high concentrations despite the influence of anthropogenic inputs. The geological characteristic, assessed by Hg content in rocky fragments (parent material composition), does not show any differences between limestone and volcanic lithologies. The natural influence in soil Hg concentration is related to the physicochemical soil properties. In general, soil characteristics, particularly organic matter and clay contents, seem to contribute mostly to the greater Hg concentration in soil. Moreover, the mean Hg contents on soils that form the Balearic archipelago are much greater (sometimes twice as high) than in the volcanic soils on the Canary archipelago. A significant amount of the increased Hg content in the topsoils of the Balearics originates from pollution. The geostatistical analysis has proven essential to understand the Hg pollution and spatial relationships, whereas the maps of topsoil and rock Hg provide accurate information to identify probable pollution sources. The increase noted in surface soil Hg on the Island of Majorca is linked to emissions from the nearby coal-fired power plant.

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