

Mercury soil pollution on Spanish islands: Methods to assess Hg input

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Abstract

The purpose of this study was to quantitatively characterise and to provide a basic understanding of mercury concentrations in soils in order to distinguish the “natural” mercury contribution from that of human-induced pollution in two Spanish archipelagos. The Canary Islands are an archipelago formed by 7 islands of volcanic origin. They are located in the Atlantic Ocean to the southwest of Spain, near the Tropic of Cancer and the western Moroccan coastline. The Balearics (limestones) are formed by 4 islands located to the east of the Iberian Peninsula and to the extreme west of the Mediterranean Sea. This study uses geostatistical methods to assess mercury concentration in topsoil, as opposed to its content in the original matter. The level of mercury was higher in topsoil than rocky fragments, specifically in the Balearics where the mean mercury content was 61 µg/kg in topsoil and 11 µg/kg in rocky fragments. Maps of the spatial distribution indicate various areas with high top/rock mercury content that are linked to emissions from the nearby thermal power plant (Es Murterar). A significant portion of the increased mercury content in the Majorca island topsoil probably originates from atmospheric deposition.

Key Words

Mercury, soil pollution, heavy metals, geostatistics, spatial variability.

Introduction

Mercury is not abundant in nature, although its presence in soils poses an important risk (Mark and Ralph 2001). The naturally occurring concentration of mercury in arable soil depends primarily on the geological parent material. However, it has become widespread as a result of many industrial practices that often cause enrichment. Human activities, including combustion of fossil fuels, waste incineration, among others, have significantly increased the emission of Hg into the atmosphere. Mercury pollution is a major worldwide environmental problem with serious immediate and long-term implications for human health. In general, mercury accumulations in soils are associated with atmospheric deposition (Engle *et al.* 2005). The anthropogenic emission of Hg is about 60–80% of global Hg emissions. Mercury is an extremely volatile metal that can remain present in the atmosphere for between 0.5 and 2 years before being deposited in soil (Navarro *et al.* 1993), and may then be transported over long distances. Thermal power plants are an important source of mercury emissions. Coal-burning power plants are the largest single source of mercury pollution, and the only major source that governments do not regulate (Coequyt and Willes 1999). The “Mercury Falling” study found that an estimated 49 tons of mercury are emitted directly into the air by hundreds of coal-burning power plants in the U.S. each year (Coequyt and Willes 1999).

The characterisation of spatial variability is essential to achieve a better understanding of the complex relationships among soil properties, environmental factors and soil pollution. Geostatistical techniques, such as kriging, incorporate the spatial characteristics of current data into the statistical estimation, which classical statistical approaches ignore (Korre 1999; Lin 2002). One example of geostatistics applications to soil science is the estimation and mapping of some heavy metals by the existing spatial dependence between observations (Goovaerts 1997).

Materials and methods

Soil samples

The sampling scheme was based on an 8x8 km grid. Soil samples were collected in 2007. Each sample was defined as a composite made up of 21 sub-samples collected with the Eijkelkamp soil sampling kit from the upper 25 cm of soil in a cross pattern. Further details can be found in Rodríguez Martín *et al.* (2006).

Analytical methods

A standard soil analysis was carried out and soil texture was determined for each sample. Total Hg (THg) analyses were performed using a direct Hg analyzer (DMA80, an atomic absorption spectrophotometer, Milestone, Wesleyan University, Middletown, CT, USA). The results of this detection system were previously validated for solid and liquid matrices (EPA 7473). A calcareous loam soil, BCR-141 R, obtained from the European Commission Community Bureau of Reference, was used as a certified reference material to check the accuracy of the method. All the materials used for the Hg analysis in this study were acid-washed with 10% HNO₃ and carefully rinsed with ultrapure water (Milli-Q system, Bedford, MA). The limits of quantification (LOQ) and detection (LOD) were 0.6 µg/kg and 0.24 µg/kg, respectively.

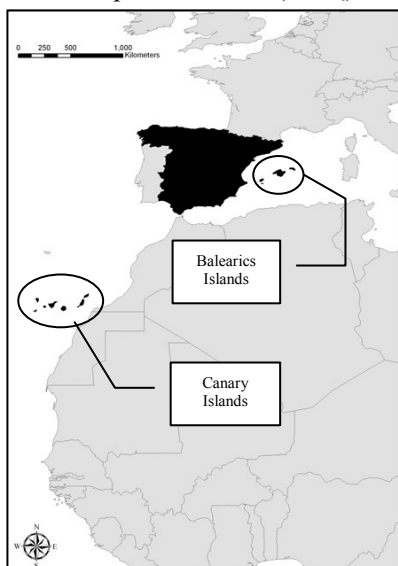


Figure 1. Location of two Spanish archipelagos. Study area.

Geostatistical analysis

A semivariogram was developed to establish the degree of spatial continuity of mercury among the data points and to establish the range of spatial dependence. The variogram γ is calculated using the relative locations of the samples (Lin, 2002) defined as (1):

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

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 .

The spherical model was used to fit the experimental semivariogram, and soil and rocky mercury contents were mapped by ordinary kriging (OK). There are many different models and kriging algorithms, most of which are reviewed in Goovaerts (1999) with references to soil applications. Textbooks (Gressie 1991; Goovaerts 1997; Kanevski and Maignan 2004) offer further detailed geostatistical methods.

Results and discussion

The statistics of the mercury contents are summarised in Table 1. The mercury topsoil concentration in this study fall between 12 and 350 µg/kg (mean 61 µg/kg) in the Balearics, and between 3 and 159 µg/kg (mean 33 µg/kg) in the Canary islands. The normal range in soils is 10–500 µg/kg (Alloway 1995). Using 4090 samples, Wu *et al.* (1991) established Hg levels of 100 µg/kg for natural or pristine areas, and of 200 µg/kg for agricultural and pastoral areas. In general, 300 µg/kg is the threshold value at which toxicity symptoms may occur. This critical value is exceeded only in two samples from the Balearics, and only seven samples are higher than 200 µg/kg.

Table 1. Statistical summary of Hg concentrations (in µg/kg).

		No. samples	Mean	Median	Stan. Dev.	1 st Qu.	3 rd Qu.	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

Stan. Dev: Standard deviation. 1st Qu, 3rd Qu: first and third quartile. P90, P95 and P99 percentiles = P 90, P 95 and P 99, respectively.

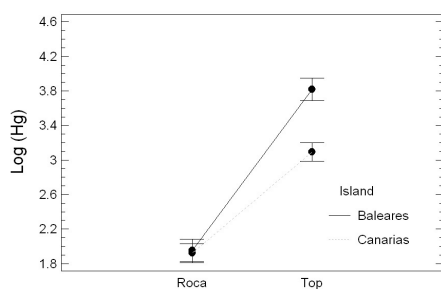
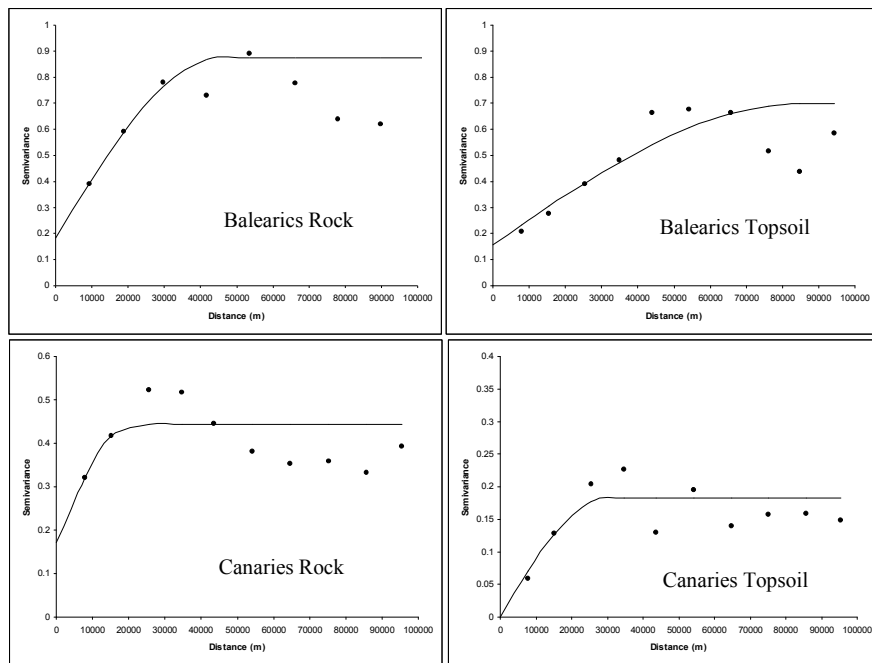


Figure 2. Top and rock mercury content in two

are considered to be strong and stable (Liu *et al.* 2003). Furthermore, mobility and retention are strongly affected by soil pH and carbonates.

The mercury in rock (original matter) is similar in both the Canaries (mean 9 µg/kg) and the Balearics (mean 11 µg/kg) (Figure 2), although it has different lithologies. The concentration ranges in rocky fragments do not present high values. In general, mercury contents tend to be higher in soils than in rock. Mercury contents usually tend to be higher in soils with high contents of clay and/or organic matter (Rodríguez Martín *et al.* 2006) due to the capacity of clay mineral to absorb cations. Organic carbon increases the binding capacity of soil for metals (Boluda 1988; Chen *et al.* 1999); this effect is due to the cation exchange capacity of organic material (Di Giulio and Ryan 1987). Complexes between Hg and organic matter

The spherical model was used to fit the experimental semivariograms (Figure 3). Spatial variation in the mercury content of rocky fragments can be attributed to inherent geographical properties and to geochemical processes that correspond to both mineralogical structures and a bedrock influence.



Variations in relation to the Hg concentration in topsoil can be largely attributed to major human perturbations such as industrialisation, agricultural practices, urban development, and a long list of many industrial practices.

In this study, ordinary kriging was used to map the mercury contents in rock and soil samples. The top/rock mercury content ratio (Figure 4) indicates three areas of high concentration levels.

Figure 3. Semivariogram for the topsoil and rock mercury values.

Soil contamination may be considered when the metal concentration in soil is eight times higher than the lithogenic content (the real geochemical baseline). These levels were higher in the Majorca island with areas whose lithogenic content is sixteen times higher. High map values were also located near the Es Murterar thermal power plant (Figure 5). This power plant used coal as fuel. Coal-burning power plants are an important source of mercury emissions (Coequyt and Willes 1999).

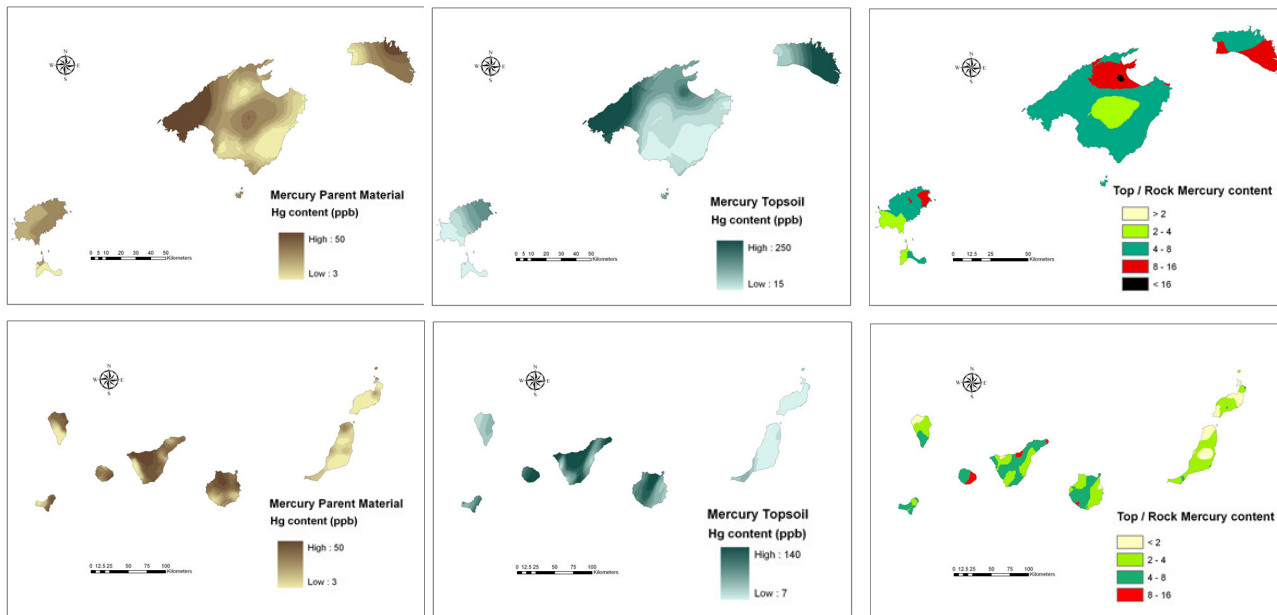


Figure 4. Kriging maps of the mercury content in top soil and parent material. Map showing

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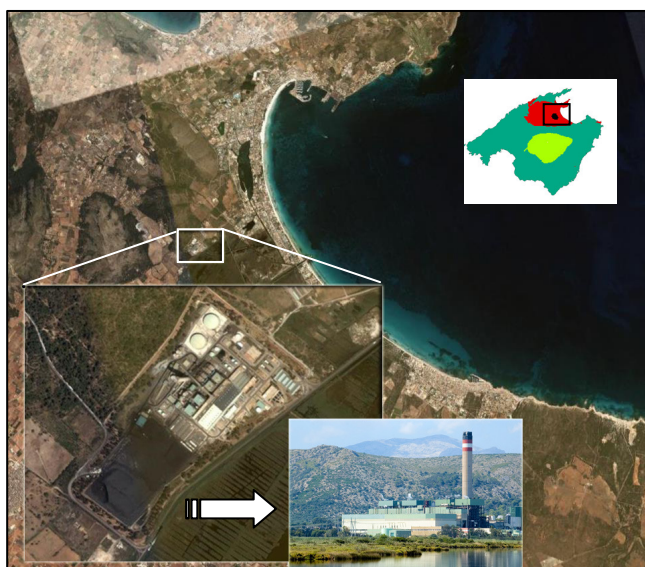


Figure 5. Es Murterar thermal power plant (Majorca).

Conclusion

A geostatistical analysis has been essential to understand the mercury pollution and spatial relationships.

The top/rock mercury content ratio was higher in Majorca (Balearics). A significant portion of the increased mercury content in topsoils of the Balearics originated from the Es Murterar thermal power plant. The specific amount of mercury cannot be determined on the basis of the data collected in this research, but this power plant is an important source of mercury pollution.

However, the soil of this Mediterranean region is principally calcareous, with an alkaline pH and a low organic matter, thereby helping to minimise the effect of mercury content.

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