Trends in soil mercury stock associated with pollution sources on a Mediterranean island (Majorca, Spain)

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Graphical Abstract

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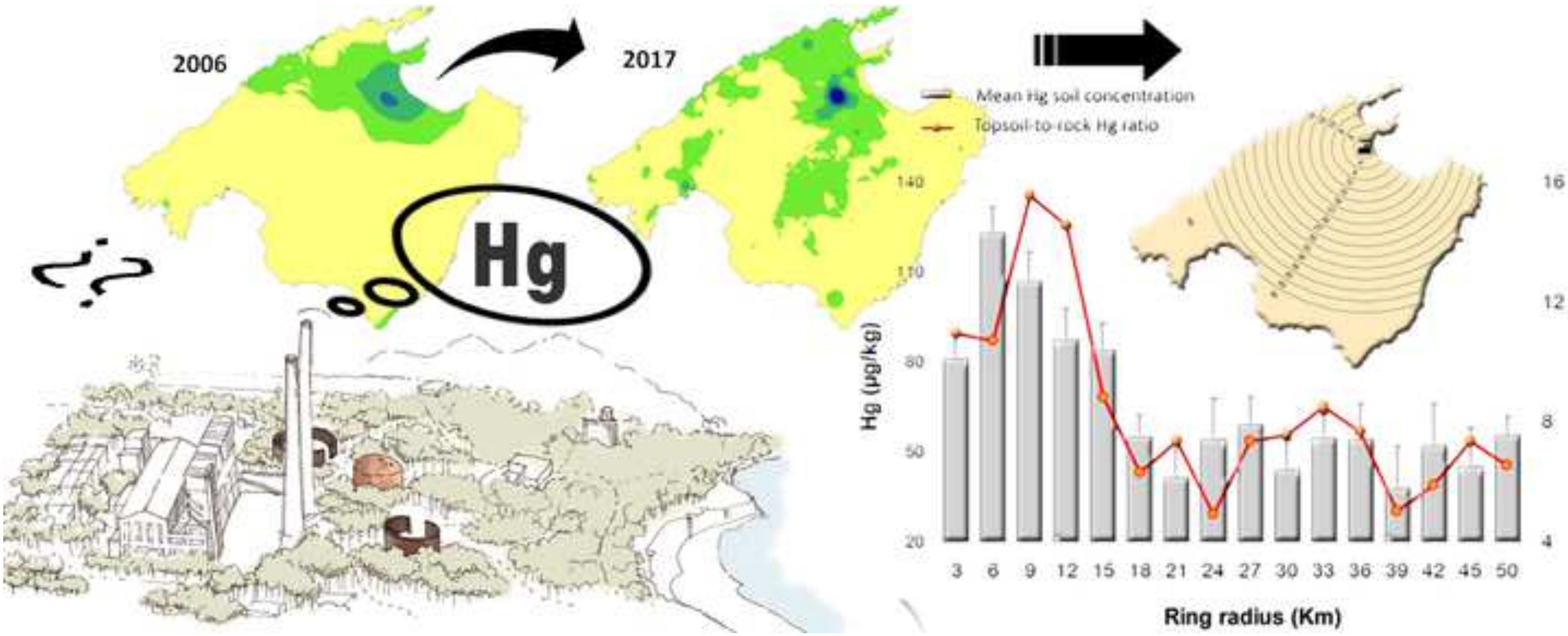

Abstract

Hg is a global concern given its adverse effects on human health, food security and the environment, and it requiring actions to identify major local Hg sources and to evaluate pollution. Our study provides the first assessment of Hg stock trends on the entire Majorca surface, identifying major Hg sources by studying the spatiotemporal soil Hg variation at two successive times (2006 and 2016-17). The Hg soil concentration ranged from 14 to 258 μg kg^{-1} (mean 52.40 μg kg^{-1}). Higher concentrations (over 100 μg kg^{-1}) were found in two areas: (i) close to the Alcudia coal-fired power plant; (ii) in the city of La Palma. During the 11-year, the total Hg stock in Majorcan soil increased from 432.96 tons to 493.18 tones (14% increase). Based on a block kriging analysis, soil Hg enrichment due to power plant emissions was clearly detectable on a local scale (i.e. a shorter distance than 18 km from the power plant). Nonetheless, a significant island-wide Hg increase due to diffuse pollution was reported. This result could be extrapolated to other popular tourist destinations in the Mediterranean islands where tourism has increased in recent decades In short, more than 60 tons of Hg have accumulated on Majorca island in 11 years.

Capsule

Spatial patterns provided the first assessment of Hg stored trends on the entire Majorca surface showed than 60 tons of Hg have accumulated on this island in 11 years

Keywords:

Soil Hg enriched; Spatial-temporal analysis; Coal-fired power plant; Hg pollution; Mediterranean soil

Highlights:

- We analysed Hg soil spatial variability on the Majorca Island
- We found a high Hg concentration near the coal-fired power plant on Majorca
- We associate this effect with spatial patterns of Hg deposition on a local scale
- We found that most emitted Hg was deposited at distances less than 15 km
- We estimated that the Hg increase on the entire island in the last 11 years was 60 t

1. INTRODUCTION

Mercury (Hg) pollution is an environmental problem which, according to the World Health Organization in 2017 (Raj and Maiti, 2019), poses a global threat. The UN's International Chemical Safety Programme indicates that Hg is one of the six worst pollutants on our planet (Keeler et al., 2006). Hg toxicity is associated with adverse effects on most living organisms, including humans, especially neurological damage (Beckers and Rinklebe, 2017; Wang et al., 2020; Zhang and Wong, 2007). Globally accumulated Hg in soil is estimated to be 250–1,000 Gg (Raj and Maiti, 2019). Although between 2,200 and 4,000 tons of Hg are emitted to the atmosphere every year (Wu et al., 2016), about 60–80% of global Hg emissions come from anthropogenic sources (Rodriguez Martin et al., 2014). According to O'Connor et al. (2019) anthropogenic emissions of Hg to the environment being on the order of 2 Gg per year. Volatilization from soil to atmosphere is considered transcendent (During et al., 2009; Rinklebe et al., 2010) and soil temperature or soil water content are considered important factors on dynamics of the total gaseous mercury (Rinklebe et al., 2010), although human activities, such as fossil combustion (Kelepertzis and Argyraki, 2015b; Lv and Liu, 2019; Rodriguez Martin et al., 2014), mining and smelting processes (Beckers and Rinklebe, 2017; Gutiérrez et al., 2016 ; Odumo et al., 2014), increase Hg levels in the environment, but the most important sources of anthropogenic Hg emissions are coal-burning power plants (Li et al., 2017; Raj and Maiti, 2019; Rodríguez Martín and Nanos, 2016).

The influence and repercussion of coal-fired power plants on atmospheric Hg emissions are well-known (see "Mercury Falling" (Coequyt et al., 1999)). In fact coal-burning power plants are the main source of Hg pollution (Wang et al., 2010; Yang and Wang, 2008). Fossil fuel combustion represents approximately 60% of Hg emissions worldwide (Pacyna et al., 2006) and 26% of all Hg emissions (236 tons/year) in European electric energy plants (Pacyna et al., 2006). In Spain alone, coal–fired electric power plants lie behind 47% of all Hg emissions (López Alonso et al., 2003). Some studies (Streets et al., 2009) estimate that overall Hg emissions could increase to 96% by 2050 if new technologies are not set up to control coal–fired electric power plants. Hg measurements in tree rings also show a continuous increase in atmospheric Hg levels between 1975 and the present-day (Clackett et al., 2018). Conversely, research carried out by EU GMOS (Global Mercury Observation System) estimate scenarios with an 85% reduction in Hg emissions by 2035 (Pacyna et al., 2016), which indicates a decrease of up to 50% deposition in the Northern Hemisphere compared to 2013. This trend will the result of the EU Mercury Strategy and the requirements set by the Minamata Convention. It will agree with what the European Commission estimates for the future, and with other research works that have indicated lowering Hg accumulation rates in the last few decades (Corella et al., 2017) in the Western Mediterranean and fewer anthropogenic Hg emissions in the past two decades in the Mediterranean Basin (Cinnirella et al., 2019).

On the other hand, population growth increases atmospheric deposition due to urban pollution (Mikayilov et al., 2019; Rodríguez Martín et al., 2015; Zhou and Wang, 2019). This is especially relevant in areas where a disproportionate increase in tourists has taken place in recent decades (Brtnický et al., 2020). Pollutants are directly associated with tourism because energy use, construction of new infrastructures, transport and other necessary services for tourists increase (Brtnický et al., 2020; Mikayilov et al., 2019; Saenz-de-Miera and Rosselló, 2014). The Majorca Island (Spain) is a good study area to evaluate possible environmental tourism impacts.

Majorca Island is one of the most popular tourist destinations in the Mediterranean Region. It has a population of less than 1 million people, but was visited by 13.6 million international tourists in 2019. For the Majorcan economy, although tourism generates most revenue, it also contributes to increase air pollution. Due to the high numbers of tourists, this demand makes a significant impact on environment. Saenz-de-Miera and Rosselló (2014) showed that a 1% rise in tourist visits to Majorca increased PM_{10} levels by 0.45%. Given the global nature of the Hg problem, the UN Environment Programme Minamata Convention (2017) includes provisions to reduce Hg emissions to the atmosphere (Fisher and Nelson, 2020). However, the problem in most countries underlies knowledge of Hg's sources and fate. In this regard, Coal-fired Thermal Power Plant of Alcudia is the unique source of electricity production in the island. Indeed soil is one of the most important reservoirs of Hg and can provide a record of its deposition (Rodríguez Martín and Nanos, 2016). The Majorca Island (Spain) is also good study area to evaluate the assumed Hg-enriched soil near the main coal-fired power plant, where the effect of Hg pollution is limited to the entire island.

The main goals of this study were to: i) determine the Hg stock on the Majorca Island; ii) analyse the spatial variability of soil Hg concentration in relation to the influence of human activities and land use; iii) assess the temporal changes in soil Hg in soil after 11 years; iv) examine the Hg contamination level due to coal-fired power plant activity.

2. MATERIALS AND METHODS

2.1 Study area

The Majorca Island was traditionally an agricultural region located to the extreme west of the Mediterranean Sea, whose climate is purely Mediterranean. The population of Majorca island has slightly increased in 2017 (a population of 883 000) since 2006 (population 794 000). Agriculture has become less important while tourism has developed in recent decades. In 2006 the number of tourists was 9.7 million, which increased to 19.6 million in 2017. Nowadays, this island is an extremely popular holiday destination, particularly for tourists from Germany and the UK. The International Palma de Majorca Airport is the third busiest in Spain, and was used by 25 million passengers in 2016 (29 million in 2019). Tourism and urban development have created a huge demand for services (food, energy, waste, rental vehicles, etc,) to the detriment of environmental quality. Ecologists in Action report that The Balearics, of which Majorca is the biggest island, has higher air pollution levels than those recommended by the World Health Organization (WHO). Moreover, some 150,000 people (13% of the islands' population) live in areas where air pollution exceeds the limits legally permitted in Spain (https://majorcadailybulletin.com/news/local/2016/10/27/45790/majorca-pollution-above-recommended-levels.html). Coal-fired Thermal Power Plant of Alcudia "Es Murterar" is the "most polluting" facility in the Balearics, is responsible for 27% of CO_2 emissions. Es Murterar power plant built in 1980 and later in 1997 it was expanded with one coal group more with installed capacity above 130 MW. Currently, the partial closure of this Power Plant is being considered as energy transition strategy.

2.2 Sampling

To evaluate the existing Hg concentration in soil on Majorca, 110 soil samples placed on a regular grid design were collected on this island in 2016 and 2017 (Figure 1). For each sampling site, at least 10 soil subsamples were taken from the upper 25 cm of soil. Subsamples were thoroughly mixed in the field to select 3 kg of soil. In addition, rocky fragments of ≥ 6 mm were taken to determine Hg contents in parent material. Twenty eight of the 110 soil samples were established as sentinel plots (Figure 1), and occupied the same locations where the 2006 field sampling was performed (Rodríguez Martín et al., 2009c). The 2006 plots were selected according to a systematic grid (8 km × 8 km size) on arable land (Rodríguez Martín et al., 2009c). The identical sampling and laboratory methodology (see the next section) was followed for both sampling campaigns to enable comparisons of Hg levels to be made over time without any interferences from the field or laboratory methods. Other measurements taken at the 2016-17 sampling locations include:

- Two metal cores (400 cm^3) per sampling site were driven in the top 20 cm of soil. The extracted soil samples were transported to the lab to determine soil bulk density (BD) and to obtain rocky fragments to evaluate stoniness
- Land-use classification of sampling locations. Sampling locations were classified into one of the following land-use types: Forest (pine- or oak-dominated), Annual crops, Fruit trees, Grassland, Wetland, Vineyard.

Figure 1: Map of the Majorca Island showing the soil samples and the position of the Alcudia coal-fired power plant.

2.3 Soil analytical methods

Soil samples were air-dried and sieved to obtain two samples with rocky fragments of > 6 mm and another sample of between 6 mm and 2 mm to determine coarse fragments (% mineral particles > 2 mm in diameter), and to analyse Hg in rock. A fine soil sample (< 2 mm) was used to establish Hg in topsoil. Bulk density was measured by the core method (Black and Hartge, 1986). Soil organic matter (SOM) was analysed by the Walkley–Black method. The total Hg in all the samples was determined by a direct Hg analyser (DMA80) (Rodríguez Martín et al., 2009a). The limits of detection (LOD) and quantification (LOQ) were 0.50 and 1.25 μg kg^{-1}, respectively. Certified calcareous loam soil (BCR-141 R with 0.24±0.03 mg kg^{-1} of total Hg) was employed for the analytical procedure validation of soil samples. The Hg analysis revealed a good agreement between the obtained and certified soil, and showed an average recovery of 98.7%. Three replicates per sample were analysed.

2.4 Statistical and geostatistical analyses

Descriptive statistics were initially computed for the variables measured during the 2016-17 field campaign (Hg in soil, Hg in rocky fragments, BD, etc.). The hypothesis of equality in the median Hg concentrations between different land-use types was tested by the Kruskal-Wallis test. The null hypothesis of no year effect (i.e. 2006 vs. 2016-17) was tested on the median Hg concentration of the 28 coincident samples by the same statistical test.

Ordinary kriging (OK) with unique-global neighbourhood was used to generate kriging maps on a squared grid of 100 x 100 m (1 ha cells) of the following variables:

- Hg concentration (µg/kg of soil)
- Bulk density (g/cm^3)
- Fraction of coarse fragments (%)

To prepare the OK maps, spherical variogram models were adjusted to their experimental counterparts. Variogram model parameters were estimated by an iterative algorithm implemented in Isatis (Isatis, 2015). The estimation accuracy of the kriging maps was assessed through cross-validation as described in Chilés and Delfiner (1999). Briefly for cross-validation, two error indices were used to assess kriging performance: (i) the mean error (E); (ii) the variance of the standardised error ($Var(E_{st})$). With denoting Z and Z* the observed and estimated value, respectively, and σ the square root of kriging variance, the error indices can be written as:

$$\overline{E} = \frac{1}{N}\sum_{1}^{N}(Z^* - Z)$$

$$Var(E_{st}) = \frac{1}{N}\sum_{1}^{N}\left(\frac{Z^* - Z}{\sigma}\right)^2$$

Estimating the Hg stock of Majorca in 2006 and 2016-17

Let $i = 1, \dots,$ then C denotes the i-th gridded cell on Majorca. The Hg stock (kg ha^{-1}) for the i-th cell was calculated for each sampling campaign as:

$$stock_{(i)} = Hg_{(i)} \times BD_{(i)} \times D \times \left(1 - S_{(i)}\right)$$

where $Hg_{(i)}$ is the soil Hg concentration (µg kg^{-1}), $BD_{(i)}$ is BD (g cm^{-3}), $S_{(i)}$ is the proportion of the volumetric coarse fragments fraction (g 100^{-1}g) of the i-th cell estimated by the above-mentioned kriging procedure and D is soil layer thickness (25 cm). Finally, the average Hg stock was calculated as the average over the C cells of the gridded map.

2.5 Studying the effect of coal-fired power plant emissions on soil Hg

To test the assumption of a distance-dependent effect of the Alcudia power plant on Hg soil concentrations, block kriging (BK) was used. This method can be followed to estimate the average pollutant concentration over a user-specified polygonal area. The method is described in detail in several geostatistical textbooks (for instance, see Chilés and Delfiner (1999)) and has been previously used in pollution case studies (Rodriguez Martin et al., 2014; Rodríguez Martín and Nanos, 2016). Polygonal blocks (otherwise polygons) were constructed using 16 concentric circles around the power plant with variable radii from 3 km to 50 km. The intercircle polygonal areas (i.e. "rings") were then employed as blocks to estimate the average Hg concentration. Prior to estimations, blocks were discretised into several small, non-overlapping rectangular cells (100 m x 100 m cell size). Then BK was used to estimate the average Hg concentration for each ring. Finally, 95% confidence intervals (95%CI) were estimated for the block-average Hg concentration based on the estimated BK variance. The kriging neighbourhood for estimating both the block-average Hg concentrations and associated estimation variances was defined as "the soil samples lying within the ring surface, plus the soil samples lying at a distance shorter than 6 km from the ring´s edge in any direction". The statistical analyses were carried out using the XLSTAT statistical package (Addinsoft Version 2012.2.02), while ISATIS V10.0 and the Geostatistical Analyst extension of ArcMap 10 were used for the geostatistical analyses.

3. RESULTS AND DISCUSSION

3.1 Soil Hg concentrations and temporal changes in sentinel plots.

The summary statistics of the Hg concentrations and soil parameters employed to estimate Hg stock are listed in Table 1. No high concentrations were observed for the Hg concentration in rocky fragments (mean 13.57 µg kg^{-1}). Hg concentrations tended to be higher in the soils (mean 64.62 µg kg^{-1}) associated with some soil physico-chemical properties, such as organic matter or clay contents (Gruba et al., 2019; Kelepertzis and Argyraki, 2015a; Petrotou et al., 2012; Rodríguez Martín et al., 2009a), but the levels in soil were 5-fold higher than lithogenic content. Mercury contaminated soils constitute complex systems where many interdependent factors, including amount and composition of soil organic matter and clays, oxidized minerals, reduced elements, as well as soil pH and redox conditions affect Hg forms and transformation (O'Connor et al., 2019). Nevertheless, the most important Hg input on the Majorca Island can be associated with human activity. In fact in global terms, the largest Hg contributions to the environment are attributed to human anthropogenic sources (Kelepertzis and Argyraki, 2015b; Mirzaei et al., 2015; Raj and Maiti, 2019; Ravankhah et al., 2017), mainly fossil fuel combustion (Beckers and Rinklebe, 2017; Botsou et al., 2020; Fisher and Nelson, 2020; Pacyna et al., 2006).

Table 1: Soil samples and statistical summary of the 2017 descriptive soil parameter sampling.

The means soil Hg concentration in Majorcan soil (Tables 1 and 2) is similar to mainland Spanish soil (60 $\mu g\ kg^{-1}$) (Rodríguez Martín et al., 2009c), but higher than Europe topsoil Hg concentration (22 $\mu g\ kg^{-1}$) (Salminen et al., 2005). Other studies have established an Hg background level of 20 $\mu g\ kg^{-1}$ (Higueras et al., 2015) and a reference value of 25 $\mu g\ kg^{-1}$ (Gil et al., 2010) for the Spanish Mediterranean Region. This study observed that 95% soil exceeded these levels. Annual crop soils (mean 70 $\mu g\ kg^{-1}$) presented maximum Hg concentration (258 $\mu g\ kg^{-1}$) (Table 2) in agricultural areas. These high levels can be related to agricultural practices, and also to agrochemicals being constantly incorporated into some annual vegetables crops, and often abusively so (Ramos-Miras et al., 2019; Rodríguez Martín et al., 2013c). However, we were surprised to also find high Hg concentrations in forest soil (68 $\mu g\ kg^{-1}$) and holm oaks, or 69 $\mu g\ kg^{-1}$ in pinewood (Table 2). These concentration levels in forest soil are higher than for other agricultural soils on Majorca, which are associated with atmospheric pollution (Hg air pollution).

Table 2: Statistical summary of the Hg concentration in soil according to the land-use classes sampling finished in 2017.

Based on the Hg concentrations evaluated in the sentinel plots, the Hg concentration in topsoil had increased after 11 years (Table 3). In 2006, the mean Hg concentration in soil was 46.60 $\mu g\ kg^{-1}$ compared to 62.10 $\mu g\ kg^{-1}$ recorded in 2017 in the same plots. Although this increase exceeds 30%, no clear differences were found to consider it to be statistically significantly according to an ANOVA test. This finding suggests that the observed increase was not homogeneous for the island on the whole, and it is also necessary to consider that the variation in Hg soil concentration among crop types (Table 2) might be more marked than the differences found between years. Therefore, it was necessary to analyse Hg spatial variability in soil to be able to quantify the Hg increase distribution and to locate possible pollution sources on this island.

Table 3: Statistical summary of the Hg concentration (μg kg^{-1}) in the sentinel plots (28 samples)

3.2 Spatial variability and assessment of Hg stock on Majorca

Experimental semivariograms are presented in the Supplementary Material (Figure S1), where the exponential model was used to fit the semivariogram. The spatial correlation range was significantly wider for BD (8 km) or stoniness (11 km) than for Hg (4.1 km), which mainly represents the spatial variation corresponding to edaphic influence and soil structure. Evidence for human influence can be associated with soil Hg concentration due to a narrower spatial range than the mineralogical and bedrock influences. Figure 2 shows the kriging map based on the semivariogram. The quality of the prediction maps was examined by the cross-validation technique (Rodríguez Martín et al., 2007). The mean errors and the root–mean–squared standardised errors respectively came close to 0 and 1 (Table S1), which indicate the good accuracy of the kriging maps. The Hg map indicated that some areas on the Majorca Island had high concentration. This was particularly evidenced in the north-eastern part of the island, which can associated with an industrial influence (Rodríguez Martín et al., 2013b) related mainly to atmospheric deposition by the coal-burning power plant (Li et al., 2017; Lv and Liu, 2019; Raj and Maiti, 2019; Rodríguez Martín and Nanos, 2016). In addition, a small area to the east of the island near its capital also presented a high Hg soil concentration. It is known that some urban activities are associated with Hg pollution (Botsou et al., 2020; Trujillo-González et al., 2016; Zhou and Wang, 2019). Higher stoniness percentages were recorded in the north and were associated mainly with forest areas. The BD map showed a more homogeneous distribution with local variation on the shorter scale related to soil compaction (Rodríguez Martín et al., 2016; Trujillo-González et al., 2019).

Figure S1: Experimental variogram and spatial models for mercury (Hg) concentration, stoniness and bulk density (BD).

Figure 2: Spatial distribution of Hg concentration, stoniness and BD interpolated by ordinary kriging.

Hg stock (Figure 3) was computed as the product of three variables (Hg concentration, BD and fraction of coarse fragments), which were regionalised by a geostatistical approach. These maps showed Hg accumulation in soil. As we can see, the Hg stock on the island generally increased, mainly in the northeast. In 2006, the highest Hg contents were observed in the vicinity of the Alcudia coal-fired power point (Rodríguez Martín et al., 2013b) where Hg accumulation was 4 g/ha. In 2017, Hg accumulation on the island was more widely dispersed (Figure 3), although greater Hg accumulation was still observed in the same area, and the highest levels had increased from 4.0 to 6.6 g/ha during the same 11-year period. The Hg stock 2017/Hg stock 2006 ratio was used to identify these areas, which might suggest pollution inputs to evaluate temporal Hg accumulation changes. Hg accumulation in this area was evidenced, where soil Hg stock had tripled in only 11 years.

Figure 3: Maps of the soil Hg stock on the Majorca Island. Values in kg ha^{-1}.

This trend is not evidenced in our case, rather Hg stock in soil considerably increased and does not only presently derive from the power plant, but also from diffuse pollution on the island that is limited mostly to both its geographical area and polluting activity on the island. Tourism pressure, and bigger summer populations (Brtnický et al., 2020) with more than more than 13 million visitors in 2017, are associated with services rendered to tourists, such as electricity, waste management, incinerators, transport, rental vehicles, etc, which also play a key role in the rising Hg levels on the island (Saenz-de-Miera and Rosselló, 2014). Growing populations and cities are undoubtedly associated with more pollution (Kelepertzis and Argyraki, 2015b; Ravankhah et al., 2016; Rodríguez Martín et al., 2015; Trujillo-González et al., 2016). Another area with a bigger Hg stock in soil is in the vicinity of the island's capital (Palma de Majorca) as the contents quantified in 2006 had doubled in 2017. Today Palma de Majorca has a population of 400,000 inhabitants, which is almost half of the whole populating living on the island (907,000 people).

In short, the Hg stock for the Majorca Island on the whole has increased from 432.96 tons in 2006 to 493.18 tons in 2017 (Table 4). This means that more than 60 tons of Hg have accumulated on the island in 11 years. For this same period, the mean Hg deposition figure has been estimated at 33.40 µg m^{-2} yr^{-1}. This value falls within the wide range of deposition figures described by other studies. For example, Yu et al.

(2013) estimated Hg deposition to be 17.4 μg m^{-2} yr^{-1} in Adirondack Mountain (New York State, USA) with wide variability (range from 3.7 to 46.0 μg m^{-2} yr^{-1}). In midcontinental North America (Wisconsin), Swain et al. (1992) quantified Hg deposition to go from 3.7 0 μg m^{-2} yr^{-1} in 1,850 to 12.5 0 μg m^{-2} yr^{-1} in recent decades. Wang et al. (2016) assessed global Hg deposition through litterfall, which they estimated was 1,180±710 Mg yr^{-1} and ranged from 2.7 to 219.9 μg m^{-2} yr^{-1}) with a mean of 27.4 μg m^{-2} yr^{-1}, which is a similar estimate to that obtained herein. On Norwegian land based on modelled deposition according to the European Monitoring and Evaluation Programme (EMEP), Braaten et al. (2018) estimated a deposition flux of only 9.5 μg m^{-2} yr^{-1}. However, Steinnes et al. (1991) quantified 35 μg m^{-2} yr^{-1} near Oslo (Norway). Navratil et al. (2019) evaluated Hg flux trends in the Czech Republic and reported means of 45 and 32 μg m^{-2} yr^{-1}, which lowered in forest soil from 66 μg m^{-2} yr^{-1} in 2003 to 23 μg m^{-2} yr^{-1} in 2017.

Table 4: Soil mercury stock estimated from the kriging maps for 2006 and 2017.

3.3 Soil Hg and relations with pollution sources

Soil Hg concentration depends primarily on geological parent material (soil-forming factors) (Jimenez Ballesta, 2017; Papastergios et al., 2009; Rodríguez Martín et al., 2009b). The rocky fragments of Hg content can be attributed only to the geochemical processes that correspond to mineralogical structures (Rodríguez Martín et al., 2013a). The Majorca Island is formed mostly by calcareous lithologies that were formed during the Tertiary and do not present high concentration. The concentration ranges in the rocky fragments on the Majorca Island fell between 5.70 and 20.50 μg kg^{-1} (mean 13.60 μg kg^{-1}) *versus* soil concentrations (mean 64.62 μg kg^{-1}) (Table 1). The topsoil/rock Hg content ratio has been used to evaluate soil Hg enrichment. Soil Hg is considered when the metal concentration in soil is 8-fold higher than the litogenic content (Rodríguez Martín et al., 2013b). Based on the assumption of a distance-dependent effect of coal-fired power plant emissions on Hg soil concentrations, 16 concentric circles (radius of 3 km) centred on the Alcudia power plant were constructed and covered the whole island surface (Figure 4). The mean Hg concentration in soil and the topsoil/rock ratio between two consecutive areas (circles) were computed by BK (Rodriguez Martin et al., 2014).

Figure 4: Estimates of soil Hg and the soil/rock ratio computed by concentric circles in block kriging and the associated confidence intervals around the Alcudia coal-fired power plant.

The soil Hg concentration displayed a decreasing trend according to the distance to the power plant (Figure 4). The highest mean concentration was observed in the second ring (6 km) and the maximum ratio in the third ring (9 km), probably as a result of pipe height preventing fly ash from being deposited on the power plant itself. Soil Hg was 15-fold higher than the lithogenic content near the power plant, which suggests major local enrichment due to emissions. The Hg accumulation in the vicinity of power plants has been reported in many studies (Li et al., 2017; Lv et al., 2019; Nóvoa-Muñoz et al., 2008; Rodríguez Martín and Nanos, 2016; Yang and Wang, 2008) and is linked with the carbon Hg content used in power plants (Rodriguez Martin et al., 2014; Wang et al., 2010). These levels were higher according to the power plant energy capacity (Nóvoa-Muñoz et al., 2008), especially in power plants over 1,000 MW (Rodríguez Martín and Nanos, 2016). On Majorca, with a capacity to generate 218 MW, the maximum soil Hg value was 258 μg kg^{-1} (Table 1). On the Spanish mainland, soil concentrations over 1,000 μg kg^{-1} have been reported near similar coal combustion power plants in Castellón (1650 MW), Aboño (921 MW) or Soto de Ribera (1481 MW) (Rodríguez Martín and Nanos, 2016). Other studies have also reported soil concentrations above 1,000 μg kg^{-1} in the Baoji Power Plant of China (Yang and Wang, 2008), 1,600 μg kg^{-1} in another Chinese power plant (Yuan et al., 2010) and 2,100 μg kg^{-1} in the Serbian Nikola Tesla power plant (Dragović et al., 2013).

To summarise, coal-burning power plants are a relevant source of Hg emissions (Coequyt et al., 1999; Furl and Meredith, 2011; Wang et al., 2010; Yang and Wang, 2008) that often cause Hg enrichment in soils associated with atmospheric deposition (Li et al., 2017; Lv et al., 2019; Rodríguez Martin et al., 2018). Hg volatilised during coal combustion comes into contact with fly ash which, given its large specific area, is finally enriched before escaping stack. This ash is deposited near power plants (Keeler et al., 2006; Li et al., 2017; Rodriguez Martin et al., 2014). According to Figure 4, the effect of the Alcudia coal-fired power plant on soil is limited to distances < 18 km, which is a similar range to that observed in other studies (Li et al., 2017; Nanos et al., 2015; Rodríguez Martín and Nanos, 2016). In this way, Hg concentrations in soil increase compared to the contribution from weathering rocks. The present study shows that the Alcudia power plant is the main local pollution source on the Majorca Island. Its local influence on Hg soil concentration rapidly decreases with distance, but diffuse pollution can affect the whole island by increasing Hg accumulation in soil through atmospheric deposition.

4 CONCLUSIONS

Spatial patterns provided valuable information to quantify and evaluate Hg stock trends. In line with the results of this study, we conclude that soil Hg levels have substantially increased on the Majorca Island due to human activities. Interpolated maps show that Hg concentration in topsoil has doubled in the vicinity of the Alcudia coal-fired power plant in 11 years. Although the degree of pollution is high, spatial patterns revealed that the most widely emitted Hg is deposited at distances less than 18 km. However, the effects of the Hg emissions from the coal-burning power plant are stronger every year and Hg deposition can be hazardous in the future if a rising trend persists.

A significant influence of tourism on the island's Hg contamination has been proved. Population growth during holiday seasons increases atmospheric deposition by rendering necessary services to tourists and related activities. In short, more than 60 tons of Hg have accumulated on this island in 11 years. Soil contamination on the Majorca Island is expected to grow, which will have a negative impact on local ecosystems. More environmental awareness is necessary in both the energy and tourism sectors. According to the UN Sustainable Development Goals (SDG) and the 2020 Environmental Action Programme motto, "Living well, within the limits of our planets" in the EU policy action, we hope that measures will be taken to conserve and protect this island from increased pollution, which will involve taking actions to reduce both the number of tourists and atmospheric deposition from the coal-fired power plant. Presently certain technology, such as activated carbon injection, can reduce emissions by 90%.

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Figure 1

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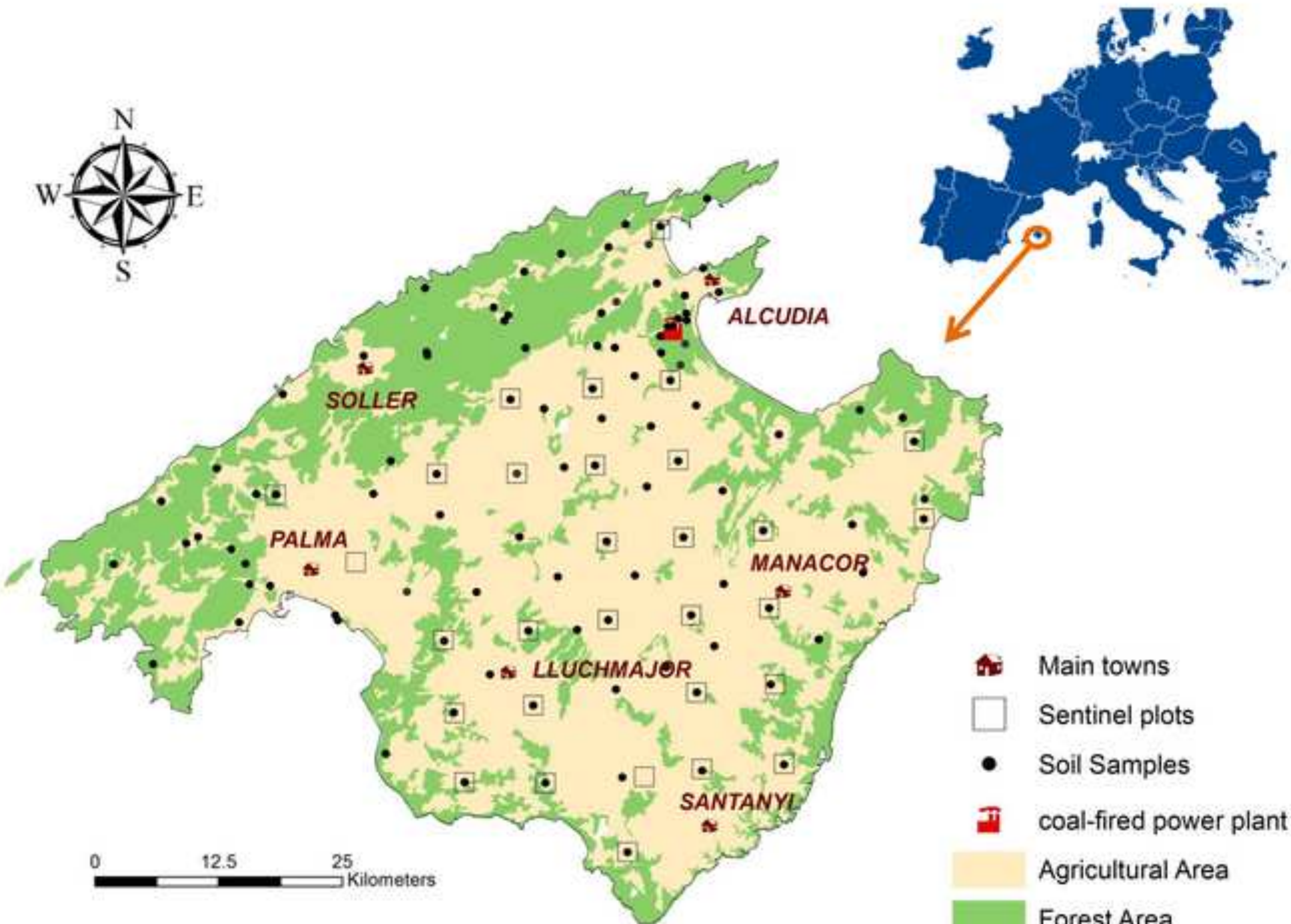

Figure 2 Click here to access/download;Figure;Figure 2.jpg

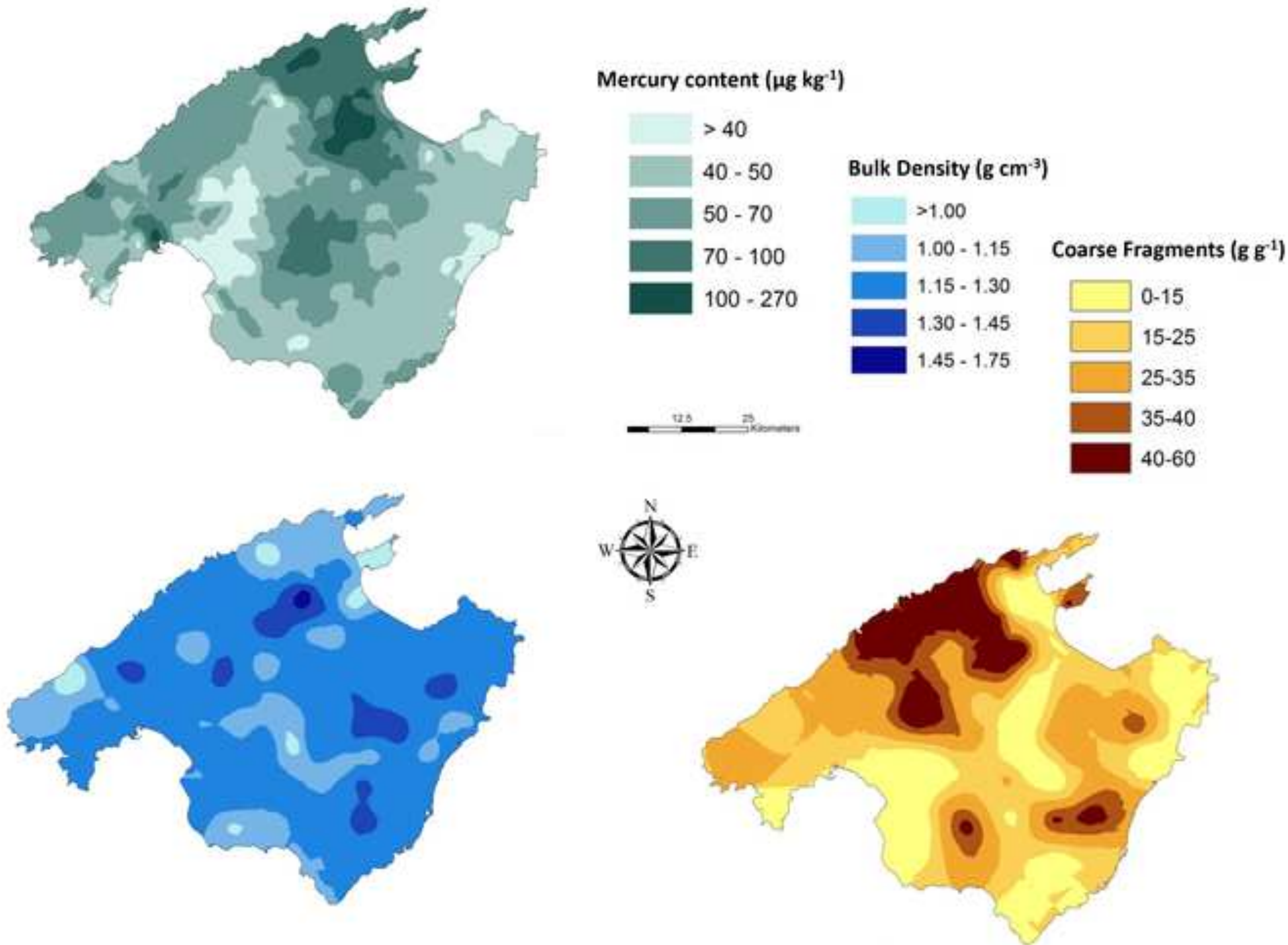

Figure 3

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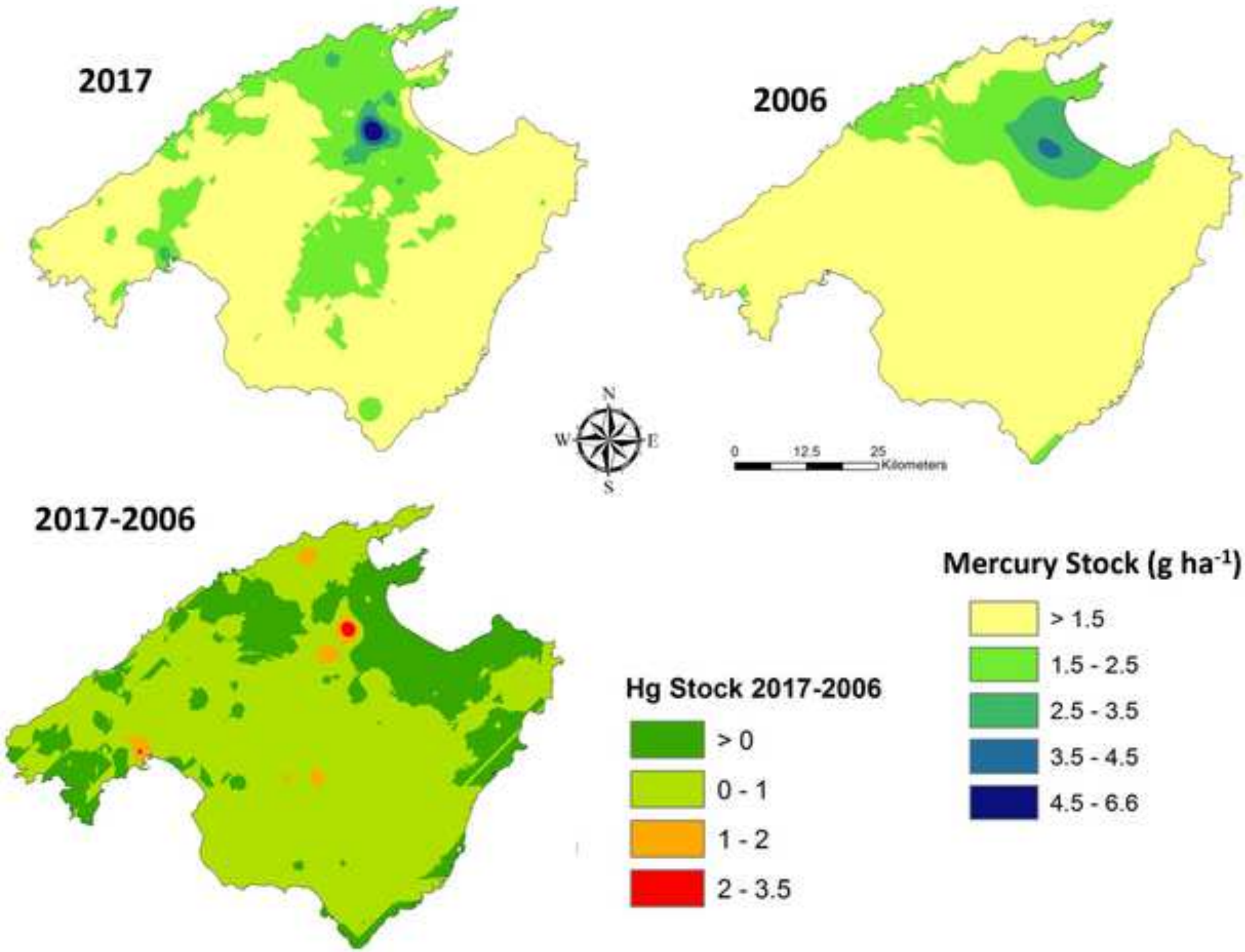

Figure 4

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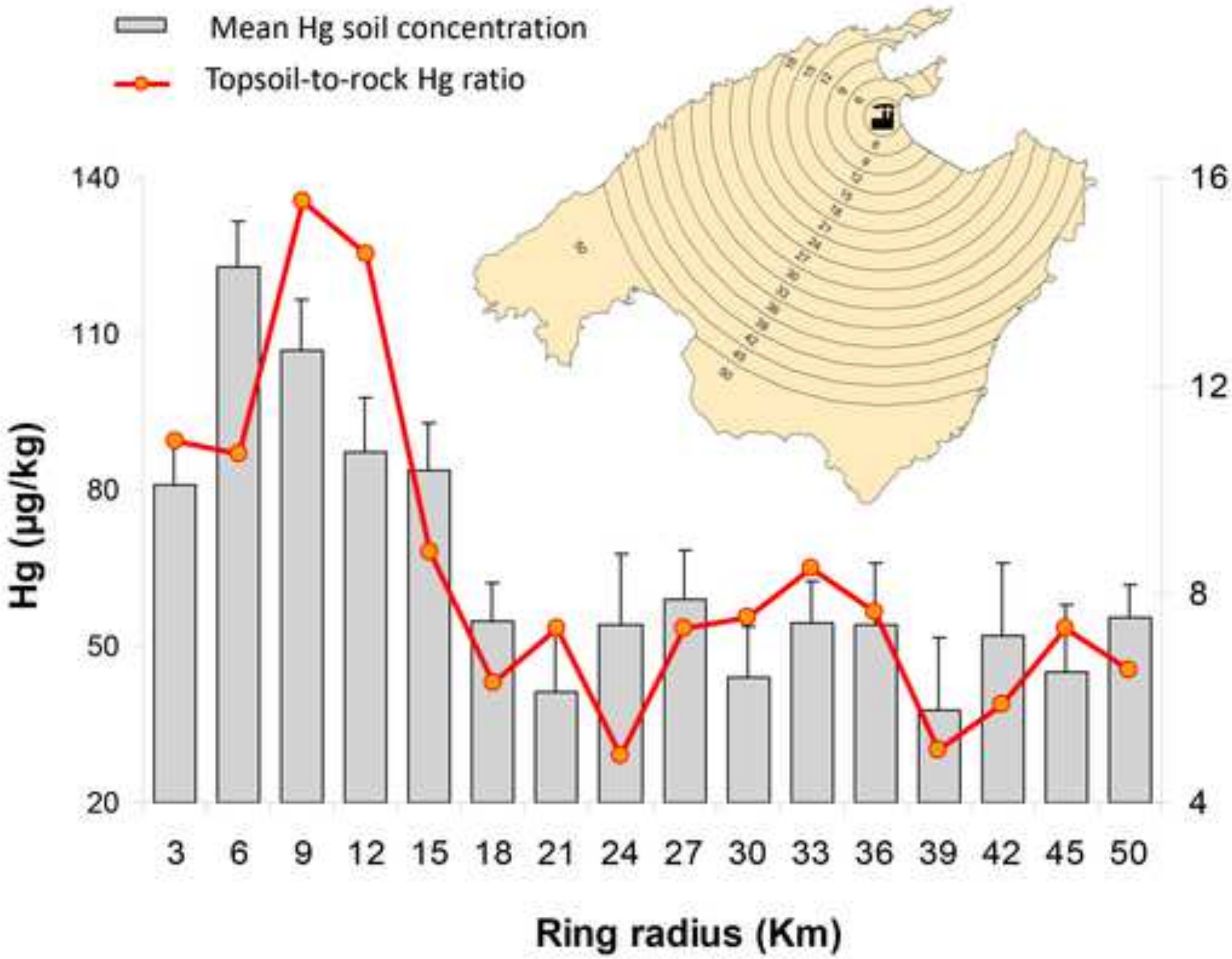

Table 1: Soil samples and statistical summary of the 2017 descriptive soil parameter sampling.

Soil parameter	**No. Samples**	**Mean**	**Median**	**SD**	**Min**	**Max**	**3rd Qu**
Topsoil Hg (µg kg^{-1})	107	64.62	52.39	36.87	13.85	258.04	78.40
Bulk density (BD)	89	1.181	1.180	0.169	0.655	1.691	1.290
Stoniness (%)	89	25.80	22.98	15.01	2.42	59.73	34.08
Rock Hg (µg kg^{-1})	86	13.57	8.32	13.14	1.62	71.14	16.37
SOC (%C)	110	2.62	2.00	1.83	0.81	12.51	3.19

Table 2: Statistical summary of the Hg concentration in soil according to the land-use classes sampling finished in 2017.

Landuse	**No. Samples**	**Mean**	**Median**	**SD**	**Min**	**Max**	**3rd Qu**
Annual crops	31	70.25	58.10	45.83	24.18	258.04	80.52
Fruit trees	19	55.19	48.29	21.84	20.55	100.54	69.15
Vineyard	2	33.69	33.69	10.86	26.01	41.37	37.53
Grassland	10	57.48	44.73	32.39	33.90	142.89	61.83
Forest (holm oak)	9	68.41	77.95	32.84	31.12	128.06	87.03
Forest (pinewood)	32	69.40	59.58	38.98	13.85	162.12	97.15
Wetland (natural Park)	4	53.74	47.67	22.94	33.61	86.01	61.32

Qu quartile; SD standard deviation.

Table 3: Statistical summary of the Hg concentration (µg kg^{-1}) in the sentinel plots (28 samples)

	2006	2016	Significant differences
Mean	46.58	62.09	P=0.161 (ANOVA). ns
Median	39.33	47.27	P=0.026 (Kruskal–Wallis test).*
SD	38.75	42.86	
Min.	17.33	20.55	
Max.	229.53	226.60	
3rd Qu	52.42	72.43	

Significant differences between years are shown in Medians (Kruskal–Wallis test), no differences are observed between the means (ANOVA test).

Table 4: Soil mercury stock estimated from the kriging maps for 2006 and 2017.

	2017	**2006**
Mean (kg/ha)	1.36	1.20
SD	0.45	0.55
Min	0.39	0.54
Max	6.67	4.06
Total Hg Stock (tons)	493.18	432.96

Total island surface is 3620km^2 (362043 ha). Temporary change in the total stock is estimated in 60.2 tons

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

CRediT author statement

José Antonio Rodríguez Martin: Conceptualization, Methodology, Writing, Writing - Review & Editing, Supervision. **Carmen Gutiérrez**: Conceptualization, Methodology, Writing, Funding acquisition. **Miguel Escuer**: Methodology, Writing, Investigation. **Marina Martín-Dacal**: Methodology, Writing, Investigation. **José Joaquín Ramos-Miras**: Validation, Writing, Investigation. **Luis Roca-Perez**: Validation, Writing, Investigation. **Rafael Boluda**: Validation, Writing, Investigation. **Nikos Nanos**: Formal analysis, Methodology, Investigation, Software

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Figure S1

Table S1

Trends in soil mercury stock associated with pollution sources on a Mediterranean island (Majorca, Spain)

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Abstract

~~Mercury~~Hg is a global concern given its adverse effects on human health, food security and the environment, and it requiring actions to identify major local Hg sources and to evaluate pollution. Our study provides the first assessment of Hg stock trends on the entire Majorca surface, identifying~~We identified~~ major Hg sources ~~on the Majorca Island~~ by studying the spatiotemporal soil Hg variation at two successive times (2006 and 2016-17). The Hg soil concentration ranged from 14 to 258 $\mu g\ kg^{-1}$ (mean 52.40 $\mu g\ kg^{-1}$). Higher concentrations (over 100 $\mu g\ kg^{-1}$) were found in ~~three~~ two areas: (i) close to the Alcudia coal-fired power plant; (ii) in the city of L~~l~~a Palma~~; in the northeastern forest areas of this island~~. During the 11-year~~ period between samplings~~, the total Hg stock in Majorcan soil increased from 432.96 tons to 493.18 tones (14% increase). Based on a block kriging analysis, soil Hg enrichment due to power plant emissions was clearly detectable on a local scale (i.e. a shorter distance than 18 km from the power plant). Nonetheless, ~~the present study also highlights~~ a significant island-wide Hg increase ~~in soil Hg content~~ due to diffuse pollution was reported. This result could be extrapolated to other popular tourist destinations in the Mediterranean islands where tourism has increased in recent decades ~~motivated by increased tourism~~ In short, more than 60 tons of Hg have accumulated on Majorca island in 11 years.

Capsule

Spatial patterns provided the first assessment of Hg stored trends on the entire Majorca surface showed than 60 tons of Hg have accumulated on this island in 11 years

Keywords:

Soil ~~mercury~~Hg enriched; Spatial-temporal analysis; Coal-fired power plant; ~~Mercury~~Hg pollution; Mediterranean soil

Highlights:

- We analysed Hg soil spatial variability on the Majorca Island
- We found a high Hg ~~content~~concentration near the coal-fired power plant on Majorca
- We associate this effect with spatial patterns of Hg deposition on a local scale
- We found that most emitted ~~mercury~~Hg was deposited at distances less than 15 km
- We estimated that the Hg increase on the entire island in the last 11 years was 60 t

1. INTRODUCTION

Mercury (Hg) pollution is an environmental problem which, according to the World Health Organization in 2017 (Raj and Maiti, 2019), poses a global threat. The UN's International Chemical Safety Programme indicates that Hg is one of the six worst pollutants on our planet (Keeler et al., 2006). Hg toxicity is associated with adverse effects on most living organisms, including humans, especially neurological damage (Beckers and Rinklebe, 2017; Wang et al., 2020; Zhang and Wong, 2007). Globally accumulated Hg in soil is estimated to be 250–1,000 Gg (Raj and Maiti, 2019). Although between 2,200 and 4,000 tons of Hg are emitted to the atmosphere every year (Wu et al., 2016), about 60–80% of global Hg emissions come from anthropogenic sources (Rodriguez Martin et al., 2014). According to O'Connor et al. (2019) anthropogenic emissions of Hg to the environment being on the order of 2 Gg per year. Volatilization from soil to atmosphere is considered transcendent (During et al., 2009; Rinklebe et al., 2010) and -soil temperature or soil water content are considered important factors on dynamics of the total gaseous mercury (Rinklebe et al., 2010), although ~~H~~human activities, such as fossil combustion (Kelepertzis and Argyraki, 2015b; Lv and Liu, 2019; Rodriguez Martin et al., 2014), mining and smelting processes (Beckers and Rinklebe, 2017; Gutiérrez et al., 2016 ; Odumo et al., 2014), increase Hg levels in the environment, but the most important sources of anthropogenic Hg emissions are coal-burning power plants (Li et al., 2017; Raj and Maiti, 2019; Rodríguez Martín and Nanos, 2016).

The influence and repercussion of coal-fired power plants on atmospheric Hg emissions are well-known (see "Mercury Falling" (Coequyt et al., 1999)). In fact coal-burning power plants are the main source of Hg pollution (Wang et al., 2010; Yang and Wang, 2008). Fossil fuel combustion represents approximately 60% of Hg emissions worldwide (Pacyna et al., 2006) and 26% of all Hg emissions (236 tons/year) in European electric energy plants (Pacyna et al., 2006). In Spain alone, coal–fired electric power plants lie behind 47% of all Hg emissions (López Alonso et al., 2003). Some studies (Streets et al., 2009) estimate that overall Hg emissions could increase to 96% by 2050 if new technologies are not set up to control coal–fired electric power plants. Hg measurements in tree rings also show a continuous increase in atmospheric Hg levels between 1975 and the present-day (Clackett et al., 2018). Conversely, research carried out by EU GMOS (Global Mercury Observation System) estimate scenarios with an 85% reduction in Hg emissions by 2035 (Pacyna et al., 2016), which indicates a decrease of up to 50% deposition in the Northern Hemisphere compared to 2013. This trend will the result of the EU Mercury Strategy and the requirements set by the Minamata Convention. It will agree with what the European Commission estimates for the future, and with other research works that have indicated lowering Hg accumulation rates in the last few decades (Corella et al., 2017) in the Western Mediterranean and fewer anthropogenic Hg emissions in the past two decades in the Mediterranean Basin (Cinnirella et al., 2019).

On the other hand,

Ppopulation growth increases atmospheric deposition due to urban pollution (Mikayilov et al., 2019; Rodríguez Martín et al., 2015; Zhou and Wang, 2019). This is especially relevant in areas where a disproportionate increase in tourists has taken place in recent decades (Brtnický et al., 2020). Pollutants are directly associated with tourism because energy use, construction of new infrastructures, transport and other necessary services for tourists increase (Brtnický et al., 2020; Mikayilov et al., 2019; Saenz-de-Miera and Rosselló, 2014). The Majorca Island (Spain) is a good study area to evaluate possible environmental tourism impacts.

Majorca This islandIsland is one of the most popular tourist destinations in the Mediterranean Region. It has a population of less than 1 million people, but was visited by 13.6 million international tourists in 2019. For the Majorcan economy, although tourism generates most revenue, it also contributes to increase air pollution. Due to the high numbers of tourists, this demand makes a significant impact on environment. Saenz-de-Miera and Rosselló (2014) showed that a 1% rise in tourist visits to Majorca increased PM_{10} levels by 0.45%. Given the global nature of the Hg problem, the UN Environment Programme Minamata Convention (2017) includes provisions to reduce Hg emissions to the atmosphere (Fisher and Nelson, 2020). However, the problem in most countries underlies knowledge of Hg's sources and fate. In this regard, Coal-fired Thermal Power Plant of Alcudia is the unique source of electricity production in the island. Indeed soil is one of the most important reservoirs of Hg and can provide a record of its deposition (Rodríguez Martín and Nanos, 2016). The Majorca Island (Spain) is also good study area to evaluate the assumed Hg-enriched soil near the main coal-fired power plant, where the effect of Hg pollution is limited to the entire island.

The main goals of this study were to: i) determine the Hg stock on the Majorca Island; ii) analyse the spatial variability of soil Hg ~~content~~concentration in relation to the influence of human activities and land use; iii) assess the temporal changes in soil Hg in soil after 11 years; iv) examine the Hg contamination level due to coal-fired power plant activity.

2. MATERIALS AND METHODS

2.1 Study area

The Majorca Island was traditionally an agricultural region located to the extreme west of the Mediterranean Sea, whose climate is purely Mediterranean. The population of Majorca island has slightly increased in 2017 (a population of 883 000) since 2006 (population 794 000). Agriculture has become less important while tourism has developed in recent decades. In 2006 the number of tourists was 9.7 million, which increased to 19.6 million in 2017. Nowadays, this island is an extremely popular holiday destination, particularly for tourists from Germany and the UK. The International Palma de Majorca Airport is the third busiest in Spain, and was used by 25 million passengers in 2016 (29 million in 2019). Tourism and urban development have created a huge demand for services (food, energy, waste, rental vehicles, etc,) to the detriment of environmental quality. Ecologists in Action report that The Balearics, of which Majorca is the biggest island, has higher air pollution levels than those recommended by the World Health Organization (WHO). Moreover, some 150,000 people (13% of the islands' population) live in areas where air pollution exceeds the limits legally permitted in Spain (https://majorcadailybulletin.com/news/local/2016/10/27/45790/majorca-pollution-above-recommended-levels.html). Coal-fired Thermal Power Plant of Alcudia "Es Murterar" is the "most polluting" facility in the Balearics, is responsible for 27% of CO_2 emissions. Es Murterar power plant built in 1980 and later in 1997 it was expanded with one coal group more with installed capacity above 130 MW. Currently, the partial closure of this Power Plant is being considered as energy transition strategy.

2.2 Sampling

To evaluate the existing Hg concentration in soil on Majorca, 110 soil samples placed on a regular grid design were collected on this island in 2016 and 2017 (Figure 1). For each sampling site, at least 10 soil subsamples were taken from the upper 25 cm of soil.

Subsamples were thoroughly mixed in the field to select 3 kg of soil. In addition, rocky fragments of ≥ 6 mm were taken to determine Hg contents in parent material. Twenty eight of the 110 soil samples were established as sentinel plots (Figure 1), and occupied the same locations where the 2006 field sampling was performed (Rodríguez Martín et al., 2009c). The 2006 plots were selected according to a systematic grid (8 km × 8 km size) on arable land (Rodríguez Martín et al., 2009c). The identical sampling and laboratory methodology (see the next section) was followed for both sampling campaigns to enable comparisons of Hg levels to be made over time without any interferences from the field or laboratory methods. Other measurements taken at the 2016-17 sampling locations include:

- Two metal cores (400 cm^3) per sampling site were driven in the top 20 cm of soil. The extracted soil samples were transported to the lab to determine soil bulk density (BD) and to obtain rocky fragments to evaluate stoniness
- Land-use classification of sampling locations. Sampling locations were classified into one of the following land-use types: Forest (pine- or oak-dominated), Annual crops, Fruit trees, Grassland, Wetland, Vineyard.

Figure 1: Map of the Majorca Island showing the soil samples and the position of the Alcudia coal-fired power plant.

2.3 Soil analytical methods

Soil samples were air-dried and sieved to obtain two samples with rocky fragments of > 6 mm and another sample of between 6 mm and 2 mm to determine coarse fragments (% mineral particles > 2 mm in diameter), and to analyse Hg in rock. A fine soil sample (< 2 mm) was used to establish Hg in topsoil. Bulk density was measured by the core method (Black and Hartge, 1986). Soil organic matter (SOM) was analysed by the Walkley–Black method. The total Hg in all the samples was determined by a direct Hg analyser (DMA80) (Rodríguez Martín et al., 2009a). The limits of detection (LOD) and quantification (LOQ) were 0.50 and 1.25 µg kg^{-1}, respectively. Certified calcareous loam soil (BCR-141 R with 0.24±0.03 mµg kg^{-1} of total Hg) was employed for the analytical procedure validation of soil samples. The Hg analysis revealed a good agreement between the obtained and certified soil, and showed an average recovery of 98.7%. Three replicates per sample were analysed.

2.4 Statistical and geostatistical analyses

Descriptive statistics were initially computed for the variables measured during the 2016-17 field campaign (Hg in soil, Hg in rocky fragments, BD, etc.). The hypothesis of equality in the median Hg concentrations between different land-use types was tested by the Kruskal-Wallis test. The null hypothesis of no year effect (i.e. 2006 vs. 2016-17) was tested on the median Hg concentration of the 28 coincident samples by the same statistical test.

Ordinary kriging (OK) with unique-global neighbourhood was used to generate kriging maps on a squared grid of 100 x 100 m (1 ha cells) of the following variables:

- Hg concentration (μg/kg of soil)
- Bulk density (g/cm^3)
- Fraction of coarse fragments (%)

To prepare the OK maps, spherical variogram models were adjusted to their experimental counterparts. Variogram model parameters were estimated by an iterative algorithm implemented in Isatis (Isatis, 2015). The estimation accuracy of the kriging maps was assessed through cross-validation as described in Chilés and Delfiner (1999). Briefly for cross-validation, two error indices were used to assess kriging performance: (i) the mean error (E); (ii) the variance of the standardised error ($Var(E_{st})$). With denoting Z and Z* the observed and estimated value, respectively, and σ the square root of kriging variance, the error indices can be written as:

$$\overline{E} = \frac{1}{N}\sum_{1}^{N}(Z^* - Z)$$

$$Var(E_{st}) = \frac{1}{N}\sum_{1}^{N}\left(\frac{Z^* - Z}{\sigma}\right)^2$$

Estimating the Hg stock of Majorca in 2006 and 2016-17

Let $i = 1, \ldots,$ then C denotes the i-th gridded cell on Majorca. The Hg stock (kg ha^{-1}) for the i-th cell was calculated for each sampling campaign as:

$$stock_{(i)} = Hg_{(i)} \times BD_{(i)} \times D \times \left(1 - S_{(i)}\right)$$

where $Hg_{(i)}$ is the soil Hg concentration (μg kg^{-1}), $BD_{(i)}$ is BD (g cm^{-3}), $S_{(i)}$ is the proportion of the volumetric coarse fragments fraction (g 100^{-1}g) of the i-th cell estimated by the above-mentioned kriging procedure and D is soil layer thickness (25 cm). Finally, the average Hg stock was calculated as the average over the C cells of the gridded map.

2.5 Studying the effect of coal-fired power plant emissions on soil Hg

To test the assumption of a distance-dependent effect of the Alcudia power plant on Hg soil concentrations, block kriging (BK) was used. This method can be followed to estimate the average pollutant concentration over a user-specified polygonal area. The method is described in detail in several geostatistical textbooks (for instance, see Chilés and Delfiner (1999)) and has been previously used in pollution case studies (Rodriguez Martin et al., 2014; Rodríguez Martín and Nanos, 2016). Polygonal blocks (otherwise polygons) were constructed using 16 concentric circles around the power plant with variable radii from 3 km to 50 km. The intercircle polygonal areas (i.e. "rings") were then employed as blocks to estimate the average Hg concentration. Prior to estimations, blocks were discretised into several small, non-overlapping rectangular cells (100 m x 100 m cell size). Then BK was used to estimate the average Hg concentration for each ring. Finally, 95% confidence intervals (95%CI) were estimated for the block-average Hg concentration based on the estimated BK variance. The kriging neighbourhood for estimating both the block-average Hg concentrations and associated estimation variances was defined as "the soil samples lying within the ring surface, plus the soil samples lying at a distance shorter than 6 km from the ring´s edge in any direction". The statistical analyses were carried out using the XLSTAT statistical package (Addinsoft Version 2012.2.02), while ISATIS V10.0 and the Geostatistical Analyst extension of ArcMap 10 were used for the geostatistical analyses.

3. RESULTS AND DISCUSSION

3.1 Soil Hg ~~content~~concentrations and temporal changes in sentinel plots.

The summary statistics of the Hg ~~content~~concentrations and soil parameters employed to estimate Hg stock are listed in Table 1. No high ~~values were~~concentrations were observed for the Hg concentration in rocky fragments (mean 13.57 μg kg^{-1}). Hg ~~content~~concentrations tended to be higher in the soils (mean 64.62 μg kg^{-1}) associated with some soil physico-chemical properties, such as organic matter or clay contents (Gruba et al., 2019; Kelepertzis and Argyraki, 2015a; Petrotou et al., 2012; Rodríguez Martín et al., 2009a),~~,~~ but the levels in soil were 5-fold higher than lithogenic content. Mercury contaminated soils constitute complex systems where many interdependent factors, including amount and composition of soil organic matter and clays, oxidized minerals, reduced elements, as well as soil pH and redox conditions affect Hg forms and transformation (O'Connor et al., 2019). Nevertheless, ~~T~~the most important Hg input on the Majorca Island can be associated with human activity. In fact in global terms, the largest Hg contributions to the environment are attributed to human anthropogenic sources (Kelepertzis and Argyraki, 2015b; Mirzaei et al., 2015; Raj and Maiti, 2019; Ravankhah et al., 2017), mainly fossil fuel combustion (Beckers and Rinklebe, 2017; Botsou et al., 2020; Fisher and Nelson, 2020; Pacyna et al., 2006).

Table 1: Soil samples and statistical summary of the 2017 descriptive soil parameter sampling.

The means soil Hg ~~content~~concentration in Majorcan soil (Tables 1 and 2) is similar to mainland Spanish soil (60 µg kg^{-1}) (Rodríguez Martín et al., 2009c), but higher than Europe topsoil Hg ~~content~~concentration (22 µg kg^{-1}) (Salminen et al., 2005). Other studies have established an Hg background level of 20 µg kg^{-1} (Higueras et al., 2015) and a reference value of 25 µg kg^{-1} (Gil et al., 2010) for the Spanish Mediterranean Region. This study observed that 95% soil exceeded these levels. Annual crop soils (mean 70 µg kg^{-1}) presented maximum Hg ~~values~~concentration (258 µg kg^{-1}) (Table 2) in agricultural areas. These high levels can be related to agricultural practices, and also to agrochemicals being constantly incorporated into some annual vegetables crops, and often abusively so (Ramos-Miras et al., 2019; Rodríguez Martín et al., 2013c). However, we were surprised to also find high Hg ~~content~~concentrations in forest soil (68 µg kg^{-1}) and holm oaks, or 69 µg kg^{-1} in pinewood (Table 2). These concentration levels in forest soil are higher than for other agricultural soils on Majorca, which are associated with atmospheric pollution (Hg air pollution).

Table 2: Statistical summary of the Hg concentration in soil according to the land-use classes sampling finished in 2017.

Based on the Hg ~~content~~concentrations evaluated in the sentinel plots, the Hg concentration in topsoil had increased after 11 years (Table 3). In 2006, the mean Hg ~~content~~concentration in soil was 46.60 µg kg^{-1} compared to 62.10 µg kg^{-1} recorded in 2017 in the same plots. Although this increase exceeds 30%, no clear differences were found to consider it to be statistically significantly according to an ANOVA test. This finding suggests that the observed increase was not homogeneous for the island on the whole, and it is also necessary to consider that the variation in Hg soil ~~content~~concentration among crop types (Table 2) might be more marked than the differences found between years. Therefore, it was necessary to analyse Hg spatial variability in soil to be able to quantify the Hg increase distribution and to locate possible pollution sources on this island.

Table 3: Statistical summary of the Hg concentration (μg kg^{-1}) in the sentinel plots (28 samples)

3.2 Spatial variability and assessment of Hg stock on Majorca

Experimental semivariograms are presented in the Supplementary Material (Figure S1), where the exponential model was used to fit the semivariogram. The spatial correlation range was significantly wider for BD (8 km) or stoniness (11 km) than for Hg (4.1 km), which mainly represents the spatial variation corresponding to edaphic influence and soil structure. Evidence for human influence can be associated with soil Hg concentration due to a narrower spatial range than the mineralogical and bedrock influences. Figure 2 shows the kriging map based on the semivariogram. The quality of the prediction maps was examined by the cross-validation technique (Rodríguez Martín et al., 2007). The mean errors and the root–mean–squared standardised errors respectively came close to 0 and 1 (Table S1), which indicate the good accuracy of the kriging maps. The Hg map indicated that some areas on the Majorca Island had high ~~values~~concentration. This was particularly evidenced in the north-eastern part of the island, which can associated with an industrial influence (Rodríguez Martín et al., 2013b) related mainly to atmospheric deposition by the coal-burning power plant (Li et al., 2017; Lv and Liu, 2019; Raj and Maiti, 2019; Rodríguez Martín and Nanos, 2016). In addition, a small area to the east of the island near its capital also presented a high Hg soil concentration. It is known that some urban activities are associated with Hg pollution (Botsou et al., 2020; Trujillo-González et al., 2016; Zhou and Wang, 2019). Higher stoniness percentages were recorded in the north and were associated mainly with forest areas. The BD map showed a more homogeneous distribution with local variation on the shorter scale related to soil compaction (Rodríguez Martín et al., 2016; Trujillo-González et al., 2019).

Figure S1: Experimental variogram and spatial models for mercury (Hg) ~~content~~concentration, stoniness and bulk density (BD).

Figure 2: Spatial distribution of Hg ~~content~~concentration, stoniness and BD interpolated by ordinary kriging.

Hg stock (Figure 3) was computed as the product of three variables (Hg concentration, BD and fraction of coarse fragments), which were regionalised by a geostatistical approach. These maps showed Hg accumulation in soil. As we can see, the Hg stock on the island generally increased, mainly in the northeast. In 2006, the highest Hg contents were observed in the vicinity of the Alcudia coal-fired power point (Rodríguez Martín et al., 2013b) where Hg accumulation was 4 g/ha. In 2017, Hg accumulation on the island was more widely dispersed (Figure 3), although greater Hg accumulation was still observed in the same area, and the highest levels had increased from 4.0 to 6.6 g/ha during the same 11-year period.

The Hg stock 2017/Hg stock 2006 ratio was used to identify these areas, which might suggest pollution inputs to evaluate temporal Hg accumulation changes. Hg accumulation in this area was evidenced, where soil Hg stock had tripled in only 11 years. ~~The influence and repercussion of coal fired power plants on atmospheric Hg emissions are well known (see "Mercury Falling" (Coequyt et al., 1999)). In fact coal-burning power plants are the main source of Hg pollution (Wang et al., 2010; Yang and Wang, 2008). Fossil fuel combustion represents approximately 60% of Hg emissions worldwide (Pacyna et al., 2006) and 26% of all Hg emissions (236 tons/year) in European electric energy plants (Pacyna et al., 2006). In Spain alone, coal-fired electric power plants lie behind 47% of all Hg emissions (López Alonso et al., 2003). Some studies (Streets et al., 2009) estimate that overall Hg emissions could increase to 96% by 2050 if new technologies are not set up to control coal-fired electric power plants. Hg measurements in tree rings also show a continuous increase in atmospheric Hg levels between 1975 and the present day (Clackett et al., 2018)). Conversely, research carried out by EU GMOS (Global Mercury Observation System) estimate scenarios with an 85% reduction in Hg emissions by 2035 (Pacyna et al., 2016), which indicates a decrease of up to 50% deposition in the Northern Hemisphere compared to 2013. This trend will the result of the EU Mercury Strategy and the requirements set by the Minamata Convention. It will agree with what the European Commission estimates for the future, and with other research works that have indicated lowering Hg accumulation rates in the last few decades (Corella et al., 2017) in the Western Mediterranean and fewer~~

~~anthropogenic Hg emissions in the past two decades in the Mediterranean Basin (Cinnirella et al., 2019).~~

Figure 3: Maps of the soil ~~mercury~~Hg stock on the Majorca Island. Values in kg ha^{-1}.

This trend is not evidenced in our case, rather Hg stock in soil considerably increased and does not only presently derive from the power plant, but also from diffuse pollution on the island that is limited mostly to both its geographical area and polluting activity on the island. Tourism pressure, and bigger summer populations (Brtnický et al., 2020) with more than more than 13 million visitors in 2017, are associated with services rendered to tourists, such as electricity, waste management, incinerators, transport, rental vehicles, etc, which also play a key role in the rising Hg levels on the island (Saenz-de-Miera and Rosselló, 2014). Growing populations and cities are undoubtedly associated with more pollution (Kelepertzis and Argyraki, 2015b; Ravankhah et al., 2016; Rodríguez Martín et al., 2015; Trujillo-González et al., 2016). Another area with a bigger Hg stock in soil is in the vicinity of the island's capital (Palma de Majorca) as the contents quantified in 2006 had doubled in 2017. Today Palma de Majorca has a population of 400,000 inhabitants, which is almost half of the whole populating living on the island (907,000 people).

In short, the Hg stock for the Majorca Island on the whole has increased from 432.96 tons in 2006 to 493.18 tons in 2017 (Table 4). This means that more than 60 tons of Hg have accumulated on the island in 11 years. For this same period, the mean Hg deposition figure has been estimated at 33.40 μg m^{-2} yr^{-1}. This value falls within the wide range of deposition figures described by other studies. For example, Yu et al. (2013) estimated Hg deposition to be 17.4 μg m^{-2} yr^{-1} in Adirondack Mountain (New York State, USA) with wide variability (range from 3.7 to 46.0 μg m^{-2} yr^{-1}). In midcontinental North America (Wisconsin), ~~-~~Swain et al. (1992) quantified Hg deposition to go from ~~1,850 (~~3.7 0 μg m^{-2} yr^{-1}~~)~~ in ~~-~~1,850 to 12.5 0 μg m^{-2} yr^{-1}~~)~~ in recent decades. Wang et al. (2016) assessed global Hg deposition through litterfall, which they estimated was 1,180±710 Mg yr^{-1} and ranged from 2.7 to 219.9 μg m^{-2} yr^{-1}) with a mean of 27.4~~39~~ μg m^{-2} yr^{-1}, which is a similar estimate to that obtained herein. On Norwegian land based on modelled deposition according to the European Monitoring and Evaluation Programme (EMEP), Braaten et al. (2018) estimated a deposition flux of only 9.5 μg m^{-2} yr^{-1}. However, Steinnes et al. (1991) quantified 35 μg m^{-2} yr^{-1} near Oslo (Norway). Navratil et al. (2019) evaluated Hg flux trends in the Czech Republic and reported means of 45 and 32 μg m^{-2} yr^{-1}, which lowered in forest soil from 66 μg m^{-2} yr^{-1} in 2003 to 23 μg m^{-2} yr^{-1} in 2017. ~~This is the completely opposite trend to that observed in our study.~~

Table 4: Soil mercury stock estimated from the kriging maps for 2006 and 2017.

3.3 Soil Hg and relations with pollution sources

Soil ~~mercury~~Hg concentration depends primarily on geological parent material (soil-forming factors) (Jimenez Ballesta, 2017; Papastergios et al., 2009; Rodríguez Martín et al., 2009b). The rocky fragments of Hg content can be attributed only to the geochemical processes that correspond to mineralogical structures (Rodríguez Martín et al., 2013a). The Majorca Island is formed mostly by calcareous lithologies that were formed during the Tertiary and do not present high ~~values~~concentration. The concentration ranges in the rocky fragments on the Majorca Island fell between 5.70 and 20.50 μg kg^{-1} (mean 13.60 μg kg^{-1}) *versus* soil ~~content~~concentrations (mean 64.62 μg kg^{-1}) (Table 1). The topsoil/rock Hg content ratio has been used to evaluate soil Hg enrichment. Soil ~~metal~~ Hg is considered when the metal concentration in soil is 8-fold higher than the litogenic content (Rodríguez Martín et al., 2013b). Based on the assumption of a distance-dependent effect of coal-fired power plant emissions on Hg soil ~~content~~concentrations, 16 concentric circles (radius of 3 km) centred on the Alcudia power plant were constructed and covered the whole island surface (Figure 4). The mean Hg concentration in soil and the topsoil/rock ratio between two consecutive areas (circles) were computed by BK (Rodriguez Martin et al., 2014).

Figure 4: Estimates of soil Hg and the soil/rock ratio computed by concentric circles in block kriging and the associated confidence intervals around the Alcudia coal-fired power plant.

The soil Hg concentration displayed a decreasing trend according to the distance to the power plant (Figure 4). The highest mean ~~content~~concentration was observed in the second ring (6 km) and the maximum ratio in the third ring (9 km), probably as a result of pipe height preventing fly ash from being deposited on the power plant itself. Soil Hg was 15-fold higher than the lithogenic content near the power plant, which suggests major local enrichment due to emissions. The Hg accumulation in the vicinity of power plants has been reported in many studies (Li et al., 2017; Lv et al., 2019; Nóvoa-Muñoz et al., 2008; Rodríguez Martín and Nanos, 2016; Yang and Wang, 2008) and is linked with the carbon Hg content used in power plants (Rodriguez Martin et al., 2014; Wang et al., 2010). These levels were higher according to the power plant energy capacity (Nóvoa-Muñoz et al., 2008), especially in power plants over 1,000 MW (Rodríguez Martín and Nanos, 2016). On Majorca, with a capacity to generate 218 MW, the maximum soil Hg value was 258 µg kg^{-1} (Table 1). On the Spanish mainland, soil ~~content~~concentrations over 1,000 µg kg^{-1} have been reported near similar coal combustion power plants in Castellón (1650 MW), Aboño (921 MW) or Soto de Ribera (1481 MW) (Rodríguez Martín and Nanos, 2016). Other studies have also reported soil ~~content~~concentrations above 1,000 µg kg^{-1} in the Baoji Power Plant of China (Yang and Wang, 2008), 1,600 µg kg^{-1} in another Chinese power plant (Yuan et al., 2010) and 2,100 µg kg^{-1} in the Serbian Nikola Tesla power plant (Dragović et al., 2013).

To summarise, coal-burning power plants are a relevant source of Hg emissions (Coequyt et al., 1999; Furl and Meredith, 2011; Wang et al., 2010; Yang and Wang, 2008) that often cause Hg enrichment in soils associated with atmospheric deposition (Li et al., 2017; Lv et al., 2019; Rodríguez Martin et al., 2018). Hg volatilised during coal combustion comes into contact with fly ash which, given its large specific area, is finally enriched before escaping stack. This ash is deposited near power plants (Keeler et al., 2006; Li et al., 2017; Rodriguez Martin et al., 2014). According to Figure 4, the effect of the Alcudia coal-fired power plant on soil is limited to distances < 18 km, which is a similar range to that observed in other studies (Li et al., 2017; Nanos et al., 2015; Rodríguez Martín and Nanos, 2016). In this way, Hg ~~content~~concentrations in soil increase compared to the contribution from ~~–~~weathering rocks. The present study shows that the Alcudia power plant is the main local pollution source on the Majorca Island. Its local influence on Hg soil ~~content~~concentration rapidly decreases with distance, but diffuse pollution can affect the whole island by increasing Hg accumulation in soil through atmospheric deposition.

4 CONCLUSIONS

Spatial patterns provided valuable information to quantify and evaluate Hg stock trends. In line with the results of this study, we conclude that soil Hg levels have substantially increased on the Majorca Island due to human activities. Interpolated maps show that Hg ~~content~~concentration in topsoil has doubled in the vicinity of the Alcudia coal-fired power plant in 11 years. Although the degree of pollution is high, spatial patterns revealed that the most widely emitted Hg is deposited at distances less than 18 km. However, the effects of the Hg emissions from the coal-burning power plant are stronger every year and Hg deposition can be hazardous in the future if a rising trend persists.

A significant influence of tourism on the island's Hg contamination has been proved. Population growth during holiday seasons increases atmospheric deposition by rendering necessary services to tourists and related activities. In short, more than 60 tons of Hg have accumulated on this island in 11 years. Soil contamination on the Majorca Island is expected to grow, which will have a negative impact on local ecosystems. More environmental awareness is necessary in both the energy and tourism sectors. According to the UN Sustainable Development Goals (SDG) and the 2020 Environmental Action Programme motto, "Living well, within the limits of our planets" in the EU policy action, we hope that measures will be taken to conserve and protect this island from increased pollution, which will involve taking actions to reduce both the number of tourists and atmospheric deposition from the coal-fired power plant. Presently certain technology, such as activated carbon injection, can reduce emissions by 90%.

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