

Local deposition of mercury in topsoils around coal-fired power plants: is it always true?

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Abstract Mercury (Hg) is a toxic element that is emitted to the atmosphere through human activities, mainly fossil fuel combustion. Hg accumulations in soil are associated with atmospheric deposition, while coal-burning power plants remain the most important source of anthropogenic mercury emissions. In this study, we analyzed the Hg concentration in the topsoil of the Kozani–Ptolemais basin where four coal-fired power plants (4,065 MW) run to provide 50 % of electricity in Greece. The study aimed to investigate the extent of soil contamination by Hg using geostatistical techniques to evaluate the presumed Hg enrichment around the four power plants. Hg variability in agricultural soils was evaluated using 276 soil samples from 92 locations covering an area of 1,000 km². We were surprised to find a low Hg content in soil (range 1–59 µg kg⁻¹) and 50 % of samples with a concentration lower than 6 µg kg⁻¹. The influence of mercury emissions from the four coal-fired power plants on soil was poor or virtually nil. We associate this effect with low Hg contents in the coal (1.5–24.5 µg kg⁻¹) used in the combustion

of these power plants (one of the most Hg-poor in the world). Despite anthropic activity in the area, we conclude that Hg content in the agricultural soils of the Kozani–Ptolemais basin is present in low concentrations.

Keywords Heavy metals · Soil mercury enriched · Coal-fired power plants · Mercury deposition · Geostatistics · Atmospheric pollution

Introduction

Mercury (Hg) is seen as one of the six worst pollutants of our planet according to the United Nation's International Chemical Safety Program (Keeler et al. 2006). The natural concentration of Hg in soil is generally very low and tends to remain within very narrow limits (0.1 µg l⁻¹ in fresh water, 0.03 µg l⁻¹ in seawater, and between 10 and 200 µg kg⁻¹ in soil (Adriano 2001; Tack et al. 2005) or between 0.005 and 0.06 ng m⁻³ in air) to ensure an optimum ecological equilibrium because Hg is the most toxic metal for the majority of living organisms (Cooper and Gillespie Jr 2001). Hg concentration in soil depends mainly on the composition of the parent material (Rodríguez Martín et al. 2009a) and edaphogenetic parameters (Gil et al. 2010; Lacerda et al. 2004). Nonetheless, human activities that involve emitting large quantities of Hg into the environment have dramatically increased natural concentrations (Pacyna et al. 2006a). Anthropogenic Hg emissions can be about 60–80 % of global Hg emissions, with around 50 % of anthropogenic Hg entering the global cycle (Liu et al. 2003).

According to Alloway (1995), the annual anthropogenic release of Hg on a global basis was about 3 × 10⁶ kg around the year 1900, which had increased to about three times that amount by the 1970s. Global spatial anthropogenic mercury emissions to the atmosphere in 1995 and 2000 are available in

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the Arctic Monitoring and Assessment Program (<http://amap.no/Resources/HgEmissions/>). The global inventory of Hg sources for the year 2000 was 2,200 t year⁻¹ (Pacyna et al. 2006b). Present-day anthropogenic mercury emissions to the atmosphere range from 2,200–4,000 t year⁻¹ (Kim and Kim 1999). According to Mason and Pirrone (Mason and Pirrone 2008), approximately one-third of the Hg currently emitted to the atmosphere derives from anthropogenic sources (2,503 t year⁻¹). Coal-burning power plants are an important source of anthropogenic mercury emissions (Wang et al. 2010; Yang and Wang 2008). Combustion of fossil fuels represented ~60 % of Hg emissions in 2000 (Pacyna et al. 2006b). The “Mercury Falling” study (Coequyt et al. 1999), based on the 1,200 power plants scattered around the USA, estimated that 49 t of mercury are emitted directly to the atmosphere every year. To reduce emissions, the EPA regulates mercury emissions from power plants since 2000 (Kim and Kim 1999). However, the largest coal producer and consumer in the world is China (Wang et al. 2010). Coal consumption by power generation in China has increased to 1.49 billion tons, although there are many elements of uncertainty surrounding mercury emissions for China (Wu et al. 2010). In Europe (Pacyna et al. 2006a), coal combustion in electric power plants alone contributes more than 26 % to total Hg emissions in Europe (236 t/year). In Spain alone, 47 % of total Hg emissions derive from all coal-fired power plants (López Alonso et al. 2003). Information on Hg emissions has been collected in various European countries and was carried out as part of EU projects to verify anthropogenic emission estimates (Pacyna et al. 2006a). Indeed, global mercury emissions could increase by up to 96 % by the year 2050 unless new control technologies for coal-fired power plants are deployed (Streets et al. 2009).

In general, Hg accumulation is associated with atmospheric deposition (Engle et al. 2006; Rodríguez Martín et al. 2013b). This particular kind of Hg can be located hundreds of kilometers from the emission source because it can remain in the atmosphere for as long as 2 years before being deposited (Schroeder and Munthe 1998). Although Hg released from coal combustion generates fly ash by incomplete combustion to carbon (Pavlish et al. 2003), it undergoes rapid deposition (Lindberg and Stratton 1998). Furthermore, the spatial distribution of mercury emissions is not uniform because it is dominated by coal-fired power plants (Rodríguez Martín et al. 2013a; Mason and Pirrone 2008). Coal combustion has been found to be the source of ~70 % of Hg in soil deposition near coal-burning power plants (Keeler et al. 2006; Dreher and Follmer 2004). Soil Hg contents can vary on different spatial scales depending on the source and type of pollution (Nanos and Rodríguez Martín 2012; Rodríguez Martín et al. 2009b). However, the main global driving force is the expansion of coal-fired electricity (Streets et al. 2009; Kim and Kim 1999).

The coal deposit of Eordea in the Kozani–Ptolemais basin comprises approximately 2.3 billion tons of lignite. Half the reserves have been used since the early 1960s by four large coal-fired power plants (about 4 GW) to satisfy nearly 50 % of Greece’s electricity demands. The required mean lignite amount for a 1,200-MW power station is estimated to be 54,000 t day⁻¹ (Triantafyllou 2003). This basin is also an important agricultural area in northern Greece, where mainly wheat and lucerne crops are grown. More than 150,000 people live and work in Kozani, Ptolemais, and in several villages in the basin. Industrial activity-based enrichment of main heavy metals (Cr, Ni, Cu, Cd, Pb, or Zn) has been reported in soil by atmospheric deposition (Triantafyllou 2003; Georgakopoulos et al. 2002; Petrotou et al. 2012; Samara 2005). However, Hg assessment has not been broadly studied. The purpose of this study was to quantitatively characterize mercury topsoil concentrations and to evaluate sources of variability. We aimed to investigate the extent of soil contamination by Hg, particularly by anthropogenic Hg from carbon combustion in coal-fired power plants. Topsoil samples and the Hg carbon used in the power plants were analyzed, and geostatistical techniques were used to evaluate the presumably Hg-enriched soil around the four power plants. Another objective was to provide a basic understanding of the Hg concentration in this basin to facilitate the estimates made at nonsampled locations.

Materials and methods

Study area and soil sampling

The Kozani–Ptolemais basin (1,000 km²) is located in northern Greece (Fig. 1) and presents highly heterogeneous geological composition. In the northernmost part of the study area (Fig. 1), metamorphic geological features predominate (schist and flysch in the NW and marbles in the NE). In the south, a gradual tendency for calcareous limestone is seen to dominate in conjunction with ophiolitic rocks. However, the vast majority of the study area consists of sedimentary rocks of mixed geological origins. From an environmental point of view, this region is deemed one of the most underdeveloped in Greece given its industrial activity (Stalikas et al. 1997). Smoke and fly ash from mining and coal-fired power stations cause respiratory problems among the population, mainly in the towns of Kozani (50,000 inhabitants) or Ptolemais (30,000 inhabitants).

The Kozani–Ptolemais basin is the main coal-mining area in Greece (three coal-mine complexes, with total reserves of 2.3 billion tons). Lignite production in 2003 was 55 million tons in the Lignite Centre of Western Macedonia (Adamidou et al. 2007). Lignite exploitation provides the four power stations with the fuel they require. These power plants have been gradually installed since 1956 and have generated

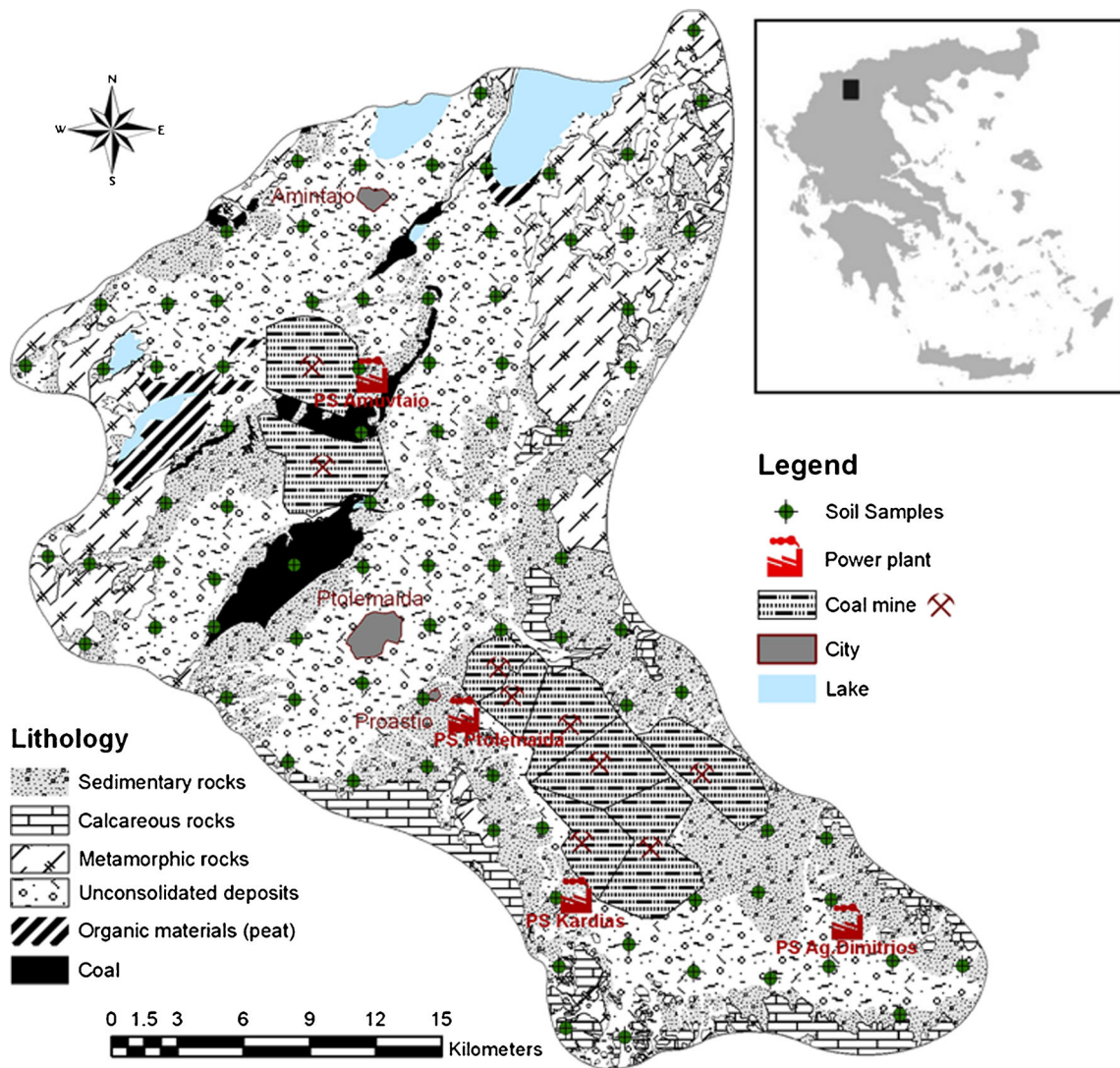


Fig. 1 Map of the study area showing the geological setting, the location of the power plants, soil samples, and the main cities and coal mines

4,065 MW (Table 1). Nowadays, 50 % of electricity in Greece is produced by the four coal-fired power plants in this area (Table 1). According to the European Pollutant Release and Transfer Register (E-PRTR), mercury emissions by these

coal-fired power stations have duplicated in the last few years. Approximately 759 kg of Hg were emitted into the atmosphere in 2007, whereas this figure increased to 1,436 kg in 2010 (Table 1). Despite their importance, no mercury data

Table 1 Production capacity and Hg contents in the coal used in power plants

Power plant	Ag. Demetrios (PP1)	Kardia (PP2)	Ptolemais (PP3)	Amynteon (PP4)
Years of construction	1984–1997	1975–1982	1959–1972	1986
Total installed capacity (MW)	1595	1250	620	600
Total Hg (kg) releases to air ^a				
Year 2007	516	69	74	100
Year 2008	932	151	81	245
Year 2009	1,020	149	78	200
Year 2010	1,020	142	55	219
Year 2011	1,010	143	58	229
Total Hg in coal ($\mu\text{g kg}^{-1}$)	1.53±0.03	22.67±1.87	24.54±2.63	–

^a Annual releases for the 2007–2011 period (E-PRTR regulation)

exist for Kozani–Ptolemais basin soils, which is a long-term sink for mercury deposition from adjacent power plants. Besides pollution, the population is concerned about not only crop production, predominantly wheat and corn, but also fruit trees and potatoes.

The basic sampling grid was square mesh with sampling points placed at intervals of 3×3 km. Based on a selection of plots of agricultural land use, a sampling plot was established at the grid nodes when at least one wheat field was visible (in the ortho-photograph) within a 600-m distance from the grid node. Sampling points were located by means of a global positioning system. At each sampling site, three subsamples were taken from the upper 20 cm of soil to obtain three soil values from each location. Soil samples were collected in winter in 2011 from 92 locations (276 subsamples) (Fig. 1). Soil samples were taken to the laboratory to be air-dried and sieved with a 2-mm grid sieve. Additionally, lignite samples were taken from three of the four mines that supply coal to the four coal-fired power plants (Table 1) to analyze mercury concentration.

Mercury analysis in soil and coal

The total Hg in all the samples was determined using a direct Hg analyzer (DMA80, atomic absorption spectrophotometer, Milestone, Wesleyan University, Middletown, CT, USA). A weighed sample (150–200 mg) was deposited into a sample boat and was then introduced into the DMA where oxygen began to flow over the sample. Decomposition oven temperature was increased: first for drying the sample, then for decomposing it. A continuous flow of oxygen was carried out on the decomposition products through a catalyst bed, where interferences were trapped. All the mercury species were reduced to elemental Hg and were then taken to a gold amalgamator where mercury was selectively trapped. The system was purged and the amalgamator was subsequently heated to release all the mercury vapors to the single-beam, fixed wavelength atomic absorption spectrophotometer. The absorbance measured at 253.7 nm was proportional to the mercury content in the sample. To determine method precision, three replicates of each sample were considered.

DMA80 provides two working ranges for Hg detection: 0–40 and 40–600 ng. Each range is calibrated independently to optimize the response over the entire dynamic range. Calibration samples containing 0, 10, 20, 30, and 40 µl of 1 or 10 ppm Hg were processed to calibrate the instrument for 0–40 and 40–400 ng, respectively. The limits of detection (LOD) and quantification (LOQ) were 0.5 and 1.25 µg kg⁻¹, respectively. The LOQ was established by the lowest calibration point. The LOD was 2.5 times lower than the LOQ when the signal-to-noise ratio was higher than 10. The analytical procedure validation of the soil and coal samples was performed with a calcareous loam soil (BCR-141 R) obtained

from the European Commission Community Bureau of Reference and a bituminous coal (NBS-1632b) from the National Bureau of Standards (USA). The Hg analysis revealed a good agreement between the obtained and the certified/recommended (0.24±0.03 µg kg⁻¹, of total Hg, for soil/70 µg Hg kg⁻¹ of total Hg, for coal) values, showing an average recovery of 98.7 and 103 % for Hg, respectively.

Statistical and geostatistical analyses

A standard statistical analysis (mean, median, standard deviation, etc.) was carried out to describe the mercury contents in the Ptolemais-Kozani basin topsoil. Significant differences between means (by lithology) were assessed through nonparametric Kruskal–Wallis tests. For the geostatistical analysis, data were log-transformed since the distribution was skewed to right. We computed the experimental variogram for the logarithm of the mean mercury concentration (i.e., averaging over the three measurements for the same sample), and we adjusted a variogram model with a semiautomatic procedure by selecting the variogram range manually (Isatis 2008).

The variogram model was used to produce the soil Hg concentration map by lognormal kriging (Chilés and Delfiner 1999). The search neighborhood for lognormal kriging was a circle with radius equal to 20 km (equal to the range of spatial correlation of the variogram model, see the following section). Back transformation of the estimated logarithmic values was used to produce a map of soil Hg (see also Chilés and Delfiner (1999) for the details of this procedure). In addition, to test the assumption of a distance-dependent effect of the power plants on the Hg concentration in soil, we constructed seven concentric circles (centered on each power plant) with a radius of $r=1,2,\dots,7$ km (Fig. 2). The mean Hg log-concentration (and the associated variance) over the area between two consecutive circles was computed by (ordinary) block kriging. This method has not been previously used for characterizing the local deposition of airborne pollutants. Block kriging has the potential to provide an estimate of the average pollutant value over a user-specified area and, as the following sections show, it can prove

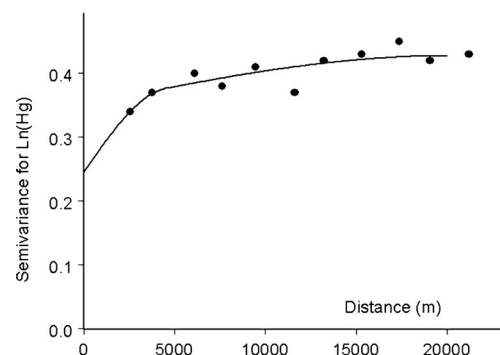


Fig. 2 Experimental variogram and model for the natural logarithm of soil Hg concentration

useful for estimating distance-dependent effects of pollutants around their emission sources. Before block kriging was used for the estimation rings around the power plants, they were discretized into 50 m×50 m regular cells (v_i). For each cell, ordinary block kriging was used by means of the following system of equations:

$$\sum_{\beta} \lambda_{\beta v} C_{\alpha\beta} + \mu = C_{\alpha v} \quad a = 1, \dots, N$$

$$\sum_{\alpha} \lambda_{\alpha} = 1$$

where $\lambda_{\beta v}$ denotes the block-kriging weight assigned to the soil Ln(Hg) concentration values lying within (or close to) ring r (to define the neighborhood, see the following paragraphs), $C_{\alpha\beta}$ is the covariance between the data points inside the kriging neighborhood, μ is the Lagrange multiplier, and $C_{\alpha v}$ is the average sample-to-block covariance.

Confidence limits (95 %) for each ring were constructed based on the block-kriging variance for ring r :

$$\sigma^2 = C_{vv} - \sum_a \lambda_a C_{\alpha v} - \mu$$

where C_{vv} is the within-block covariance (computed after the random discretization of the ring). The kriging neighborhood used for estimating the average ring Hg concentrations and the associated variance of estimation was defined by using all the samples within the ring surface augmented by the soil samples lying at a distance shorter than 3 km from the ring's edge.

Results and discussion

Soil mercury contents

The summary statistics of Hg contents in topsoils for the main lithology types are listed in Table 2. The Hg concentration in this study fell between 1 and 59 $\mu\text{g kg}^{-1}$, and 50 % of the samples were under 6 $\mu\text{g kg}^{-1}$. These mercury levels in soil are low. Worldwide mercury concentrations in soils range

between 10 and 200 $\mu\text{g kg}^{-1}$ soil (Adriano 2001; Tack et al. 2005) or, according to other studies, between 10 and 500 $\mu\text{g kg}^{-1}$ (Alloway 1995). Wu et al. (1991) using 4,090 samples established Hg levels of 100 $\mu\text{g kg}^{-1}$ for natural or pristine areas and of 200 $\mu\text{g kg}^{-1}$ for agricultural areas. In general, 300 $\mu\text{g kg}^{-1}$ is the threshold value at which toxicity symptoms may occur. Soil mercury contents of different countries are provided in Table 3, which shows large variability in concentrations depending on the area analyzed. The concentration ranges in the Kozani–Ptolemais basin did not generally present high values as the mean value (9.15 $\mu\text{g kg}^{-1}$) was lower than most values reported in the literature.

The original Hg sources common to all soils are the minerals constituting the rocks forming the soil parent material. Some investigations (Alloway 1995) have assumed that Hg levels in soil are higher in igneous and sedimentary rock types. Mercury accumulated in soils is associated with accumulation of iron and aluminum oxides (Lacerda et al. 2004). Nonetheless, we found no important differences between lithologies (Table 2). Only three samples taken in peat soil showed a higher Hg content. Mercury concentration tended to be higher in soils with high organic matter contents (Rodríguez Martín et al. 2009a) due to the capacity of clay mineral to absorb cations. Furthermore, humic substances in organic soil can serve as strong reducing and complexing agents and may influence the processes controlling the mobilization of many toxic metals, including Hg (Chen et al. 1999). In any case, the Hg contents in the peat soil of the Kozani–Ptolemais basin were not high. Arfstrom et al. (2000) found in the peat soils of Florida (USA) ranges from 117 to 300 $\mu\text{g kg}^{-1}$ (mean 209 $\mu\text{g kg}^{-1}$) and assumed that a significant portion of the increased mercury content came from the deposition of anthropogenic atmospheric mercury.

Mercury atmospheric inputs increase mercury content in soils (Lacerda et al. 2004; Liu et al. 2003). Anthropogenic emissions account for the remaining two-thirds of current worldwide mercury air emissions (Schuster et al. 2002). In Europe, 240 t of Hg were released from coal and other fossil fuels (48 %) in the year 2000 (Mason and Pirrone 2008). Coal-burning power plants are reported as being an important source of mercury emissions (Dreher and Follmer 2004;

Table 2 Statistical summary of soil Hg concentration ($\mu\text{g kg}^{-1}$)

Lithology	N.	Mean	Median	Min.	Max.	SD
Sedimentary rocks	87	10.89 (a)	8.0	3	49	8.67
Calcareous rocks	6	5.66 (b)	5.0	4	8	1.36
Metamorphic rocks	21	4.62 (b)	4.0	3	8	1.28
Unconsolidated deposits	147	8.92 (b)	6.0	1	59	9.98
Organic materials (peat)	3	13.67 (a)	13.0	13	15	1.15
Organic materials (coal)	9	4.44 (b)	4.0	3	6	1.33
Total	279	9.15	6.0	1	59	9.02

Significant differences amongst the lithology ($P < 0.01$) are indicated by different letters after the nonparametric Kruskal–Wallis test

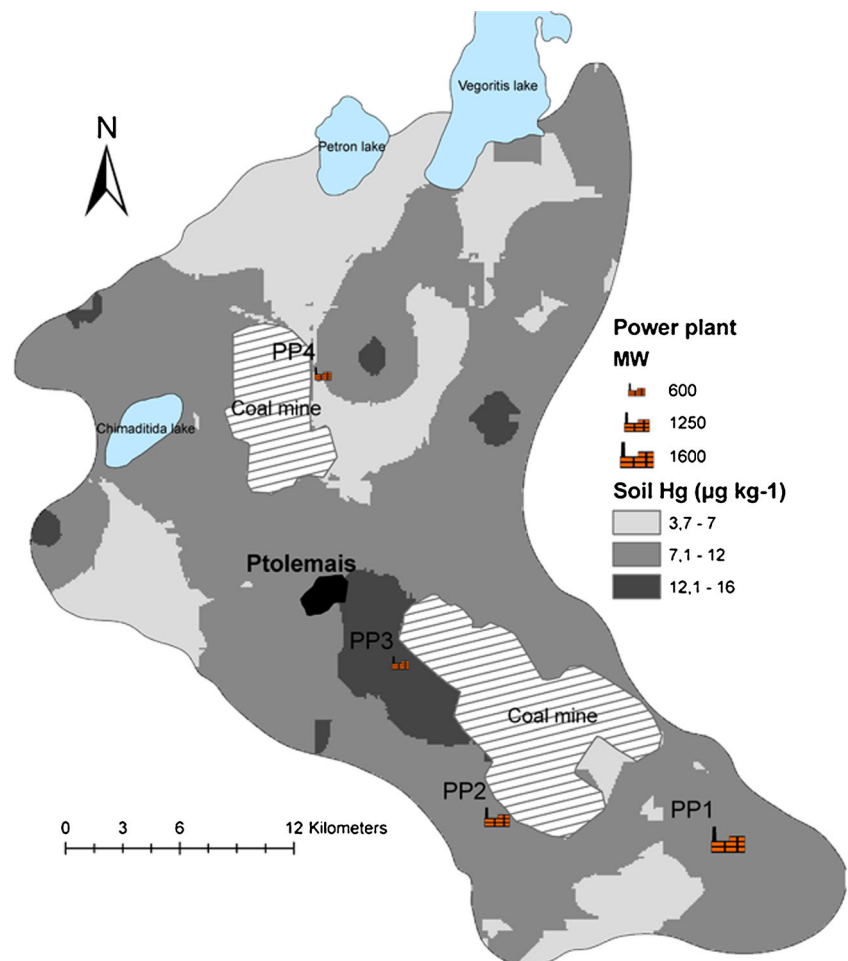
Table 3 Range and mean values of Hg contents in topsoil reported in different studies by various researchers

Site	Range	Mean ($\mu\text{g kg}^{-1}$)	Reference
Greece	25–98	68	(Haidouti et al. 1985)
Spain	1–717	35.6	(Rodríguez Martín et al. 2009a)
Belgium	30–4190	240	(Tack et al. 2005)
Taiwan	16–210	55.1	(Lin 2002)
China	20–30	65	(Li and Wu 1991) (Wu et al. 1991)
Illinois (USA)	8–123	33	(Dreher and Follmer 2004)
Mississippi (USA)	10–200	55.1	(Cooper and Gillespie Jr 2001)
Florida (USA)	0.6–430	12.6	(Chen et al. 1999)
Brazilian Amazon	10–74	33.8	(Lacerda et al. 2004)

López Alonso et al. 2003; Wang et al. 2010; Yang and Wang 2008). The “Mercury Falling” study (Coequyt et al. 1999), based on more than 1,200 power plants dotted around the USA, estimated that 49 t of mercury are emitted directly to the atmosphere every year. In Europe, coal-firing power plants are the most important individual mercury pollution sources (Pacyna et al. 2006a). Coal combustion in electric power plants alone contributes more than 26 % to the total Hg emissions in Europe (236 t year^{-1}).

The presence and accumulation of Hg in soil around power plants have been reported as being more significant in the vicinity of power plants in a number of studies (Nóvoa-Muñoz et al. 2008; Rodríguez Martín et al. 2013a; Engle et al. 2006; Wang et al. 2010; Yang and Wang 2008). Usually, increments in Hg content in soil are related with the power production capacity of these power plants, as reported in Nóvoa-Muñoz et al. (2008) for As Pontes (1,400 MW) in Galicia (NE Spain). The four coal-fired power plants in our study area generate

Fig. 3 Lognormal kriging map for soil Hg concentration



4,065 MW in all (Table 1), and according to the European Pollutant Release and Transfer Register (E-PRTR), more than 6 t of mercury have been emitted in recent years (2007–2011). The annual quantities of Hg emitted from the four coal power plants in E-PRTR data are approximate estimates of real pollution release rates and do not seem to corroborate our results on soil and carbon-feed Hg contents. We attribute this effect to the low Hg contents present in the coal used as fuel in those power plants (Table 1). The Hg concentration in coal fell by between 1.5 $\mu\text{g kg}^{-1}$ in the coal of Ag. Demetrios and 24.5 $\mu\text{g kg}^{-1}$ in the coal of Ptolemais power plant. Although it is very difficult to generalize about the mercury concentration in coal, data in the literature indicate that mercury concentrations in coals vary between 10 and 1,500 $\mu\text{g kg}^{-1}$ (Mason and Pirrone 2008) or, according to other studies, between 10 and 500 $\mu\text{g kg}^{-1}$ (Wang et al. 2010). Other estimates done in

Chinese studies (where energy production from coal combustion is the largest) indicated 220 (range 20–1,920 $\mu\text{g kg}^{-1}$) (Wang et al. 2000), 520 (Zheng et al. 2007), or 190 $\mu\text{g kg}^{-1}$ (Mason and Pirrone 2008), as reported for 1,699 coal samples in Chinese coals. In summary, despite coal combustion being the main source of mercury emissions (accounting for 60 %, or even more (Pacyna et al. 2006a), the use of coal in the Kozani–Ptolemais power plants involves low Hg contents, indicating that mercury emissions are also low.

Hg mapping and spatial relations with coal-fired power plants

The experimental variogram and the model for Ln(Hg) are presented in Fig. 2. The variogram model is a linear combination of two spherical models with ranges of 4.5 and 20 km. The spatial correlation is weak on the spatial scale studied

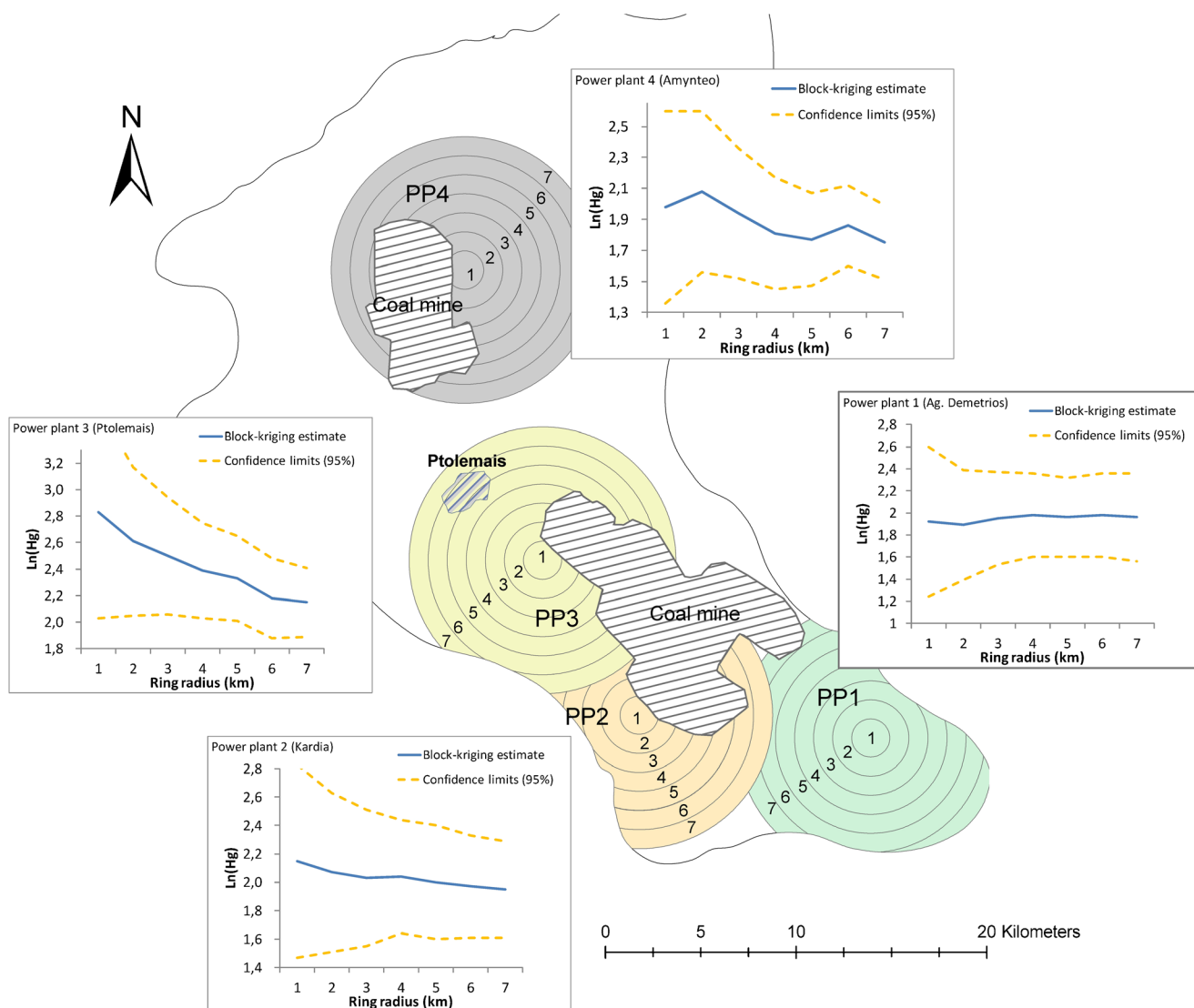


Fig. 4 Estimates of soil Ln(Hg) and the associated confidence intervals around the four power plants. Ring estimates and variances were computed by block kriging

since the nugget effect was almost 60 % of the total sill of the variogram. Probably, the spatial distribution of mercury in soil is controlled by factors acting on smaller spatial scales that are common in soil variability (soil organic matter, clay contents, physicochemical parameters, etc.). The weak spatial correlation herein reported indicates that the local deposition of airborne mercury is most likely not responsible for shaping the spatial distribution of soil Hg because, in the opposite case, we would expect a much stronger spatial autocorrelation in the sample variogram. Moreover, a low spatial correlation is exhibited since the Hg soil concentration is not linked to the main geological features of the study area. Other studies have indicated not only a stronger spatial correlation of soil mercury but also a wider spatial correlation range (Rodríguez Martín et al. 2013a).

The estimated map (by lognormal kriging) for soil Hg is presented in Fig. 3. The lowest concentration (less than $7 \mu\text{g kg}^{-1}$) is observed in the northern and the north-western parts of the study area. The highest concentration values (between 12 and $16 \mu\text{g kg}^{-1}$) are observed in the area between the Ptolemais power plant (PP3 in Fig. 3) and the city of Ptolemais. The area around the remaining power plants is not affected by Hg emission. Elsewhere, the soil around coal-fired power plants has been shown to be rich in Hg, $100\text{--}150 \mu\text{g kg}^{-1}$ in the Albufera Mallorca power plant (Rodríguez Martín et al. 2013a), $1,000 \mu\text{g kg}^{-1}$ in the Baoji Power plant of China (Yang and Wang 2008), $1,600 \mu\text{g kg}^{-1}$ in another Chinese power plant (Yuan et al. 2010), and $2,100 \mu\text{g kg}^{-1}$ in the Serbian Nikola Tesla power plant (Dragović et al. 2013). The values detected close to both the Ptolemais power plant ($12\text{--}16 \mu\text{g kg}^{-1}$) and the rest of the power plants (less than $12 \mu\text{g kg}^{-1}$) confirm the result that soil is not affected by the short-distance mercury deposition emitted from stack, most probably because the coal used in combustion is one of the most Hg-poor in the world.

The estimated Hg concentration according to distance to the power plant presents a decreasing trend in the Ptolemais and the Kardia power plants, while no clear trend is seen for the other power plants (Fig. 4). According to the confidence intervals estimated through kriging variance, the detected trend is not significant. Especially for the smaller radius rings (i.e., 1 and 2 km from stack), the standard deviation of the block-kriging estimates is very high given the small number of soil samples supporting the estimation. However, the soil Hg around the Ptolemais power station is very low and cannot be attributed to power-plant pollutant emissions. The observed enrichment might be attributed to emissions from the nearby city of Ptolemais (30,000 inhabitants) that originate from industrial and/or vehicular emissions since traffic is very close to this power plant and gasoline-powered motor vehicles may emit significant amounts of mercury (Landis et al. 2007). Previous results on the distance-dependent effect of power plants on soil Hg are contradictory, with some research works

indicating major enrichment close to the source (Rodríguez Martín et al. 2013a; Yang and Wang 2008) and others reporting either no trend at all or nonsignificant trends (Weir et al. 2010). Local mercury deposition due to power plant emissions may be linked not only to mercury content in feed coal but also to power plant characteristics and local meteorology. In any case, the power plants included in this study are fed with low Hg-content coal, and their effect on the nearby soil Hg concentration is most likely nonsignificant.

Conclusions

The Hg content in Kozani–Ptolemais basin agricultural soils is found at low concentrations in spite of the anthropic activity in the area. No differences between lithologies are shown by the geological characteristic. The soil Hg concentration is related to a natural influence in accordance with the physicochemical soil properties controlled by factors acting on spatial scales smaller than the one studied here. The soil Hg in the Kozani–Ptolemais basin is not linked to emissions from the nearby coal-fired power plant. The influence of the mercury emissions from the four coal-fired power plants on soil is low or virtually nil. The Hg concentrations in the surface soil around the power plants are also low. Indeed, only one area close to the Ptolemais power plant showed a distance-dependent trend, but this effect cannot be attributed solely on power plants emissions. The low Hg soil content and the poor spatial correlation are associated with the low mercury content deriving from power plants by atmospheric deposition. The coal used in combustion at the Ptolemais–Kozani power plants is one of the most Hg-poor in the world, indicating that mercury emissions are also low. More research is required to generalize our knowledge on mercury variation and the casual factors in the Kozani–Ptolemais basin on a local scale.

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References

- Adamidou K, Kassoli-Fournaraki A, Filippidis A, Christanis K, Amanatidou E, Tsikritzis L, Patrikaki O (2007) Chemical investigation of lignite samples and their ashing products from Kardia lignite field of Ptolemais, Northern Greece. *Fuel* 86(16):2502–2508. doi: [10.1016/j.fuel.2007.02.008](https://doi.org/10.1016/j.fuel.2007.02.008)
- Adriano DC (2001) Trace elements in terrestrial environments: biogeochemistry, bioavailability, and risks of metals. Springer Verlag, New York

- Alloway BJ (1995) Heavy metals in soils, vol Ed. 2. Blackie Academic & Professional, Netherlands
- Arfstrom C, Macfarlane A, Jones R (2000) Distributions of mercury and phosphorous in Everglades soils from water conservation area 3A, Florida, U.S.A. *Water Air Soil Pollut* 121(1–4):133–159. doi:10.1023/a:1005214908516
- Chen M, Ma LQ, Harris WG (1999) Baseline concentrations of 15 trace elements in Florida surface soils. *J Environ Qual* 28(4):1123–1181
- Chilés JP, Delfiner P (1999) Geostatistics: modeling spatial uncertainty. John Wiley & Sons Inc, New York
- Coeqyt J, Group EW, Council NRD, Network CA (1999) Mercury falling: an analysis of mercury pollution from coal-burning power plants. Environmental Working Group
- Cooper CM, Gillespie WB Jr (2001) Arsenic and mercury concentrations in major landscape components of an intensively cultivated watershed. *Environ Pollut* 111(1):67–74. doi:10.1016/s0269-7491(00)0029-4
- Dragović S, Čujić M, Slavković-Beskoski L, Gajić B, Bajat B, Kilibarda M, Onjia A (2013) Trace element distribution in surface soils from a coal burning power production area: a case study from the largest power plant site in Serbia. *Catena* 104(0):288–296. doi:10.1016/j.catena.2012.12.004
- Dreher GB, Follmer LR (2004) Mercury content of Illinois soils. *Water Air Soil Pollut* 156(1):299–315. doi:10.1023/b:wate.0000036824.07207.16
- Engle MA, Sexauer Gustin M, Johnson DW, Murphy JF, Miller WW, Walker RF, Wright J, Markee M (2006) Mercury distribution in two Sierran forest and one desert sagebrush steppe ecosystems and the effects of fire. *Sci Total Environ* 367(1):222–233. doi:10.1016/j.scitotenv.2005.11.025
- Georgakopoulos A, Filippidis A, Kassoli-Foumaraki A, Iordanidis A, Fernández-Turiel J-L, Llorens J-F, Gimeno D (2002) Environmentally important elements in fly ashes and their leachates of the power stations of Greece. *Energy Sources* 24(1):83–91. doi:10.1080/00908310252712325
- Gil C, Ramos-Miras J, Roca-Pérez L, Boluda R (2010) Determination and assessment of mercury content in calcareous soils. *Chemosphere* 78(4):409–415. doi:10.1016/j.chemosphere.2009.11.001
- Haidouti C, Skarlou V, Tsouloucha F (1985) Mercury contents of some Greek soils. *Geoderma* 35(3):251–256. doi:10.1016/0016-7061(85)90041-2
- Isatis (2008) Isatis software manual. Geovariances & Ecole des Mines de Paris, Paris
- Keeler GJ, Landis MS, Norris GA, Christianson EM, Dvonch JT (2006) Sources of mercury wet deposition in Eastern Ohio, USA. *Environ Sci Technol* 40(19):5874–5881. doi:10.1021/es060377q
- Kim K-H, Kim S-H (1999) Heavy metal pollution of agricultural soils in central regions of Korea. *Water Air Soil Pollut* 111(1–4):109–122. doi:10.1023/a:1005056310428
- Lacerda LD, de Souza M, Ribeiro MG (2004) The effects of land use change on mercury distribution in soils of Alta Floresta, Southern Amazon. *Environ Pollut* 129(2):247–255. doi:10.1016/j.envpol.2003.10.013
- Landis MS, Lewis CW, Stevens RK, Keeler GJ, Dvonch JT, Tremblay RT (2007) Ft. McHenry tunnel study: source profiles and mercury emissions from diesel and gasoline powered vehicles. *Atmos Environ* 41(38):8711–8724. doi:10.1016/j.atmosenv.2007.07.028
- Li J, Wu Y (1991) Historical changes of soil metal background values in select areas of China. *Water Air Soil Pollut* 57(1):755–761
- Lin Y-P (2002) Multivariate geostatistical methods to identify and map spatial variations of soil heavy metals. *Environ Geol* 42(1):1–10. doi:10.1007/s00254-002-0523-1
- Lindberg SE, Stratton WJ (1998) Atmospheric mercury speciation: concentrations and behavior of reactive gaseous mercury in ambient air. *Environ Sci Technol* 32(1):49–57. doi:10.1021/es970546u
- Liu R, Wang Q, Lu X, Fang F, Wang Y (2003) Distribution and speciation of mercury in the peat bog of Xiaoxing'an Mountain, northeastern China. *Environ Pollut* 124(1):39–46. doi:10.1016/s0269-7491(02)00432-3
- López Alonso M, Benedito JL, Miranda M, Fernández JA, Castillo C, Hernández J, Shore RF (2003) Large-scale spatial variation in mercury concentrations in cattle in NW Spain. *Environ Pollut* 125(2):173–181. doi:10.1016/s0269-7491(03)00073-3
- Mason R, Pirrone N (2008) Mercury fate and transport in the global atmosphere: measurements, models and policy implications, vol United Nations Environment Programme. UNEP, Rome
- Nanos N, Rodríguez Martín JA (2012) Multiscale analysis of heavy metal contents in soils: spatial variability in the Duero river basin (Spain). *Geoderma* 189–190:554–562. doi:10.1016/j.geoderma.2012.06.006
- Nóvoa-Muñoz JC, Pontevedra-Pombal X, Martínez-Cortizas A, García-Rodeja Gayoso E (2008) Mercury accumulation in upland acid forest ecosystems nearby a coal-fired power-plant in Southwest Europe (Galicia, NW Spain). *Sci Total Environ* 394(2–3):303–312. doi:10.1016/j.scitotenv.2008.01.044
- Pacyna EG, Pacyna JM, Fudala J, Strzelecka-Jastrzab E, Hlawiczka S, Panasiuk D (2006a) Mercury emissions to the atmosphere from anthropogenic sources in Europe in 2000 and their scenarios until 2020. *Sci Total Environ* 370(1):147–156. doi:10.1016/j.scitotenv.2006.06.023
- Pacyna EG, Pacyna JM, Steenhuisen F, Wilson S (2006b) Global anthropogenic mercury emission inventory for 2000. *Atmos Environ* 40(22):4048–4063. doi:10.1016/j.atmosenv.2006.03.041
- Pavlish JH, Sondreal EA, Mann MD, Olson ES, Galbreath KC, Laudal DL, Benson SA (2003) Status review of mercury control options for coal-fired power plants. *Fuel Process Technol* 82(2–3):89–165. doi:10.1016/S0378-3820(03)00059-6
- Petrotou A, Skordas K, Papastergios G, Filippidis A (2012) Factors affecting the distribution of potentially toxic elements in surface soils around an industrialized area of northwestern Greece. *Environ Earth Sci* 65(3):823–833. doi:10.1007/s12665-011-1127-4
- Rodríguez Martín J, Carbonell Martín G, López Arias M, Grau Corbí J (2009a) Mercury content in topsoils, and geostatistical methods to identify anthropogenic input in the Ebro basin (Spain). *Span J Agric Res* 7(1):107–118
- Rodríguez Martín J, Vazquez de la Cueva A, Grau Corbí J, Martínez Alonso C, López Arias M (2009b) Factors controlling the spatial variability of mercury distribution in Spanish topsoil. *Soil Sediment Contam* 18(1):30–42
- Rodríguez Martín JA, Carbonell G, Nanos N, Gutiérrez C (2013a) Source identification of soil mercury in the Spanish islands. *Arch Environ Contam Toxicol* 64:171–179
- Rodríguez Martín JA, Nanos N, Miranda J, Carbonell G, Gil L (2013b) Volcanic mercury in *Pinus canariensis*. *Naturwissenschaften* 100:739–747
- Samara C (2005) Chemical mass balance source apportionment of TSP in a lignite-burning area of Western Macedonia, Greece. *Atmos Environ* 39(34):6430–6443. doi:10.1016/j.atmosenv.2005.07.027
- Schroeder WH, Munthe J (1998) Atmospheric mercury—an overview. *Atmos Environ* 32(5):809–822. doi:10.1016/s1352-2310(97)00293-8
- Schuster PF, Krabbenhoft DP, Naftz DL, Cecil LD, Olson ML, Dewild JF, Susong DD, Green JR, Abbott ML (2002) Atmospheric mercury deposition during the last 270 years: a glacial ice core record of natural and anthropogenic sources. *Environ Sci Technol* 36(11):2303–2310. doi:10.1021/es0157503
- Stalikas CD, Chaidou CI, Pilidis GA (1997) Enrichment of PAHs and heavy metals in soils in the vicinity of the lignite-fired power plants of West Macedonia (Greece). *Sci Total Environ* 204(2):135–146. doi:10.1016/S0048-9697(97)00156-3

- Streets DG, Zhang Q, Wu Y (2009) Projections of global mercury emissions in 2050. *Environ Sci Technol* 43(8):2983–2988. doi:10.1021/es802474j
- Tack FMG, Vanhaesebroeck T, Verloo MG, Van Rompaey K, Van Ranst E (2005) Mercury baseline levels in Flemish soils (Belgium). *Environ Pollut* 134(1):173–179
- Triantafyllou A (2003) Levels and trend of suspended particles around large lignite power stations. *Environ Monit Assess* 89(1):15–34. doi:10.1023/a:1025829907390
- Wang Q, Shen W, Ma Z (2000) Estimation of mercury emission from coal combustion in China. *Environ Sci Technol* 34(13):2711–2713. doi:10.1021/es990774j
- Wang S, Zhang L, Li G, Wu Y, Hao J, Pirrone N, Sprovieri F, Ancora M (2010) Mercury emission and speciation of coal-fired power plants in China. *Atmos Chem Phys* 10(3):1183–1192
- Weir S, Halbrook R, Sparling D (2010) Mercury concentrations in wetlands associated with coal-fired power plants. *Ecotoxicology* 19(2):306–316. doi:10.1007/s10646-009-0413-3
- Wu Y, Zhou Q, Adriano DC (1991) Interim environmental guidelines for cadmium and mercury in soils of China. *Water Air Soil Pollut* 57–58(1):733–743. doi:10.1007/bf00282937
- Wu Y, Streets D, Wang S, Hao J (2010) Uncertainties in estimating mercury emissions from coal-fired power plants in China. *Atmos Chem Phys* 10(6):2937–2946
- Yang X, Wang L (2008) Spatial analysis and hazard assessment of mercury in soil around the coal-fired power plant: a case study from the city of Baoji, China. *Environ Geol* 53(7):1381–1388. doi:10.1007/s00254-007-0747-1
- Yuan C-G, Wang T-F, Song Y-F, Chang A-L (2010) Total mercury and sequentially extracted mercury fractions in soil near a coal-fired power plant. *Fresenius Environ Bull* 19(12):2857–2863
- Zheng L, Liu G, Chou C-L (2007) The distribution, occurrence and environmental effect of mercury in Chinese coals. *Sci Total Environ* 384(1–3):374–383. doi:10.1016/j.scitotenv.2007.05.037