Evidence of mercury sequestration by carbon nanotubes and nanominerals present in

agricultural soils from a coal fired power plant exhaust

Ainara Gredilla[1], Silvia Fdez-Ortiz de Vallejuelo[2,*], Azibar Rodriguez-Iruretagoiena[2], Leandro Gomez[3, 4], Marcos L.S. Oliveira[3, 4], Gorka Arana[2], Alberto de Diego[2], Juan Manuel Madariaga[2], Luis F.O. Silva[3, 4, **]

[1] Department of Applied Chemistry, Faculty of Chemistry, University of the Basque Country UPV/EHU, P.C. 2018 San Sebastian, Basque Country, Spain.

[2] Department of Analytical Chemistry, Faculty of Science and Technology, University of the Basque Country UPV/EHU, P.O. Box 644, 48080 Bilbao, Basque Country, Spain.

[3] Department of Civil and Environmental, Universidad de la Costa, Calle 58 #55-66, 080002, Barranquilla, Atlántico, Colombia.

[4] Faculdade Meridional IMED, Senador Pinheiro 304, 99070-220, Passo Fundo - RS, Brazil.

*Corresponding author at: University of the Basque Country UPV/EHU,

silvia.fernandez@ehu.eus (S. Fdez-Ortiz de Vallejuelo),

**Corresponding author at: Universidad De La Costa, felipeqma@hotmail.com (Luis F.O. Silva).

ABSTRACT

Mercury (Hg) in agricultural soils could have negative effects on the environment and the human health. The exposure to high level of Hg through different absorption pathways, such as ingestion and diet through soil-plant system could permanently damage developing foetus of animals and humans.

With the aim to assess the potential environmental and health risk and to study the behaviour and fate of Hg from agricultural soils to the environment, 47 soil samples were collected around a

thermoelectric power plant in the Santa Catarina (Brazil). The Hg concentration measured by inductively coupled plasma mass spectrometry (ICP-MS) ranged from 0.16 to 0.56 mg·kg^{-1}. The distribution obtained by kriging interpolation allowed the identification of the main pollution sources. To see the morphology and composition of soil samples, field emission scanning electron microscopy (FE-SEM) and high resolution transmission electron microscopy (HR-TEM) were used combined with energy dispersive X-ray spectroscopy (EDS), showing that the carbon nanotubes and magnetite as nanomineral contributed to Hg retention. The mentioned molecular characterization, and the low Contamination Factors (CF) values obtained, suggested that there is low risk to the food security of the agro-ecosystems area near to the CFPP in the terms of Hg inputs and contamination.

Keywords: Mercury, agricultural soils, coal fly ash, environmental risk, human health, carcinogenic risk.

1. Introduction

Due to its high toxicity to organisms and persistence in the environment mercury (Hg) has been listed as priority pollutant internationally (Echeverria et al. 2005, Wang et al. 2004). Although it is non-essential element, Hg is a potential neurotoxin when is accumulated in the central nervous system (Zagury et al. 2006). The Hg biogeochemical cycle is complex and can involve diverse environmental compartments (such as air, land and water) with natural (volcanic eruptions, weathering of the crust, etc.) or anthropogenic origin (Boening, 2000). In the environment, Hg is most commonly encountered in elemental form, as inorganic mercuric (HgII) compounds, or as monomethylmercury compounds. The most important source of mercury is the naturally occurring mineral, cinnabar (HgS). Monomethylated mercury compounds are most likely to be found in soil as a result of natural microbial transformation of inorganic mercury (Environment Canada, 2002).

Inorganic mercury may occur in three different valent states in soil depending on different factors. The organic matter (OM) is considered the most important factor for Hg biogeochemistry. Many studies have demonstrated that the high affinity of OM to Hg through the different functional groups such as hydroxy carboxylic, aromatic acids and S-containing ligands, decrease its bioavailabity and, consequently, the risk associated to it. Soil mineralogy and pH are factors to be considered too. The maximum sorption of added Hg (II) usually occurs in the pH range of 3 to5 and the fine particle size tend to contain more Hg than the coarser fractions (Xu et al., 2014).

Once on the soil Hg can have negative impact on ecosystems and human health, especially, in the case of agricultural ecosystem through various absorption pathways, such as ingestion, dermal contact, and diet through soil-plant system. The increasing agricultural intensification that is currently suffering an important part of the world has increased the inputs of agricultural machinery, fertilizer, pesticide, and irrigation water. Consequently, the quality of agricultural soils and crop is getting worse seriously. In Fact, agricultural soils are considered one of the important sources of Hg in crops and vegetables since their roots can take up Hg from soil, and transfer it to edible parts, and consequently, to humans and animals. The exposition to high levels of Hg could hurt humans´ brain, kidneys, and developing foetuses. The World Health Organization (WHO) suggested that the Provisional Tolerable Weekly Intake (PTWI) of Hg is $1,0\,\mu g \cdot kg^{-1}$ body weight (JECFA 2010). There are studies in humans that have demonstrated the human health risk for breathing, exposition or consuming of Hg, especially in the case of children (Peregrino et al. 2010). Levy et al. (2004) investigated the effect of amalgam fillings and fish consumption on urine mercury level (UHg) in children aged 4-8 years old. Using a sample of 60 children, it was concluded that children with amalgam fillings had significantly higher UHg levels than children without amalgams. Statistical analyses provide evidence of an association between elevated UHg level and young age in children with amalgam chewing surfaces. Moreno et al. (2010), found Hg concentration above the reference value in children's blood samples residing in the mining area of Taxco (Southern Mexico). In Lake Chapala (central Mexico), for example, the correlation between fish consumption and mercury concentration in hair samples from women of

child-bearing age was observed. Women of child-bearing age is a population of significant public health concern because of the potent prenatal neurotoxicity of methylmercury (Trasande et al., 2017).

In some countries, the main source of Hg emitted to the atmosphere is the coal combustion processes carried out in coal-fired power plants (CFPPs) for electricity and heat production (Rallo et al. 2012). Thus, the control of Hg at CFPPs has been one of the main objectives of the international environmental protection agencies. In response to these, coal-fired power plants have taken different measures, such as, the use of engineered solutions to capture Hg from their air emissions and/or the good mining practices prior to delivery to the CFPP (Glodek et al. 2009, Hower et al., 2010, Sekine et al. 2015, Serre et al. 2000). Good mining practices requires the reduction of pollution and waste, the conservation of natural resources, and the minimization of any potential negative environmental impacts derived from the mining activities and operations.

Moreover, the coal type used for combustion is also an important point to be considered, since depending on the coal type used for combustion, the capacity of the ashes to capture Hg is also different. Despite these steps, Hg can be present in soil samples of the surrounding of a CFPP because of the atmospheric transport by wind as wind-borne soil particles or by deposition under both dry and wet conditions. The increase of Hg in soils has been clearly observed for instance, in surrounding soil of CFPPs in Serbia (Dragović et al., 2013) and in Spain (Nóvoa-Muñoz et al., 2008). Hence, the analysis of these soil samples may provide information about the success of the corrective action to decrease the Hg emissions from the CFPPs.

In this study, we carried out an intensive survey of Hg in the agricultural soil around a CFPP and the main objectives were: *i)* to evaluate the content of Hg in soil samples, *ii)* to identify the major sources of Hg, and *iii)* to determine the mobility of Hg from the soils. With this objective, we investigated the distribution and morphology of Hg in soil samples and in the coal fly ash nanoparticles of the soils using analytical techniques such as inductively coupled plasma mass spectrometry (ICP-MS), field emission scanning electron microscopy with energy dispersive X-

ray Spectroscopy (FE-SEM-EDS) and high-resolution transmission electron microscopy with energy dispersive X-ray spectroscopy (HR-TEM-EDS).

2. Materials and methods

2.1. Study area and sampling procedures

The work is focused on agricultural soils of Santa Catalina state (Brazil). The population of Santa Catalina state (southern region of Brazil) is around 6,727.000 habitants and it is economically well-being (the GDP of Santa Catarina state was around US$ 123 billion in 2008). The state covers an area with intense agricultural, livestock, urban, mining, industrial, and leisure activities (Osório et al. 2014). The Thermoelectric Complex *Jorge Lacerda* (León-Mejía et al. 2018) is also located in the Santa Catarina state. *Jorge Lacerda* Thermal Power Plant is considered the biggest coal burning thermoelectric power plant of South American and is situated between two important cities (and rivers), Capivari de Baixo and Tubarão (Rodriguez-Iruretagoiena et al. 2015). From 32.3 billion tons of known coal reserves, Santa Catarina has more than 3.4 billion tons and, thus, it is considered the largest Brazilian Run of Mine coal producer. In fact, Thermoelectric Complex Jorge Lacerda has a total installed capacity of 857 MW and consumes about 2.9×10^6 tons of coal per year (Mariano et al. 2016, Godoya et al. 2005). For every 100 tons of coal consumed in a thermoelectric complex, is generated 42 tons of ash (Pozzobon, 1999). Around the CFPP flat lands, with average height of 9 m above sea level, are occupied by rice plantations.

As it can be seen in the Figure 1, a total of 47 soil samples were collected in the area under study (700 Km^2). The selection of the sampling sites was principally according to: *i)* the proximity to the CFPP, *ii)* the use of the soil and *iii)* the proximity to other types of polluted areas. 38 soils (code sample: *1* to *4*, *11*, *11.1*, *11.2, 16, 17* and *19* in Capivari de Baixo city; *12* to *15* in Tubarao city; *21* to *24* near Laguna, between Jaguaruna lake and sea; *25* to *28* near Congonnos and *29* to *37* near to Jaguaruna city) were collected from the agricultural (rice crops), urban and husbandry areas nearby the thermoelectric plant, and the other 9 soils (codified from *IMI01* to *IMI04*, *TRZ1*

and *TRZ2*, and *IMB01* to *IMB03*) were urban soils collected in the municipalities of Imaruí (coastal), Treze de Maio (inner) and Imbituba (coastal) far from CFPP.

Approximately 500 g of surface soil samples (~5 cm depth) were collected using plastic sampling utensils and latex gloves, put into clean plastic bags and taken to the laboratory in portable cooler boxes at 4°C, in order to avoid cross contamination or losses by adsorption during sampling, transportation and storage. Once in the laboratory, each soil sample was frozen and then lyophilized in a Cryodos apparatus from Telstar. Dried samples were sieved to assure a maximum particle size of 2 mm. Finally, the samples were kept in the refrigerator at 4°C until their analysis.

2.2. Analytical methods

The analytical determination of Hg in the soil samples were carried out following the US Environmental Pollution Agency EPA 3051A method which describes the Microwave Assisted Acid Digestion of Sediments, Sludge, Soils, and Oils. 0.5 g of soil were weighed directly into each pre-cleaned vessel in an analytical Mettler-Toledo balance AJ150 model (±0.0001 g) and 9 mL of HNO_3 and 3 mL of HCl as acid mixture was added. A first ramp of 1000W was applied during 7 min. to reach the temperature established in the method (170 °C) and then it was maintained at 800W during 4.5 min. After cooling, the acid extracts were filtered through a 0.45 μm PVDF filters and transferred to a polyethylene bottle with a final volume of 50 mL. A vessel containing the same acid mixture as used for the samples was also prepared and utilized as analytical blank and was included every ten samples. The acid extracts were diluted to 1% HNO_3 and stored at 4°C until analysis. For quality assurance purposes, soil certified reference material (SRM 2711 Montana Soil, National Institute of Standards & Technology) was analyzed in each sample batch obtaining satisfactory results. The concentrations of the Hg were determined by ICP-MS (NexION 300, Perkin Elmer, Ontario, Canada), using the external calibration method with internal standard correction (^{209}Bi). Samples were measured three times and the data were considered acceptable when RSD<10 %. The limit of detection (LOD) was calculated following

the IUPAC rules, defined as blank signal plus 3 SD, where SD is the standard deviation of 10 measurements of a blank (n=10). The LOD estimated was 0.14 mg·kg^{-1}.

In the direct analysis on the sieved samples with higher concentration of Hg (sample code: *11* and *13*) field emission scanning electron microscopy (FE-SEM; Zeiss Model ULTRA plus, for minerals/particles between 0.5 and 80 μm) and high-resolution transmission electron microscope (HR-TEM, for minerals/particles between 0.1 and 500 nm), both equipped with an Oxford energy dispersive X-ray spectrometer (EDS) for chemical analyses of individual particles following the procedure reported in previous studies, were used (Fdez-Ortiz de Vallejuelo et al. 2017, Civeira et al. 2016, Silva et al. 2011a).

FE-SEM and HR-TEM analyses of the samples and minerals included within them were carried after a water-extraction step (leaching test), as a simulation of the rain water effect on these soil samples. These analyses were essential for a complete understanding of the materials and compounds involved on the dissolution and mobilization process by the water on the soils. Thus, 1 mg of the each sample (five replicates) was mixed with 1 mL of Millipore-system water (Milli-Q water) having an electrical conductivity of 0.1–0.5 μS/cm. Samples were shaken in the dark for 4 h, then centrifuged (3000 rpm, 10 min.) and filtered (22 μm). This extraction dissolves salts and other minerals soluble in water.

The solid fraction was cold dried, suspended in acetone, pipetted on to separated lacy carbon films supported by Cu grids, and left to evaporate before inserting the sample into the FE-SEM and HR-TEM.

As far as authors know, our study is the first study that proves the evidences of encapsulated Hg by nanoparticles in soils and demonstrated the real environmental and human risk by meteorological factors such as rain water.

2.3. Statistical and kriging analysis

All statistical analyses were performed using Microsoft Excel and SPSS 13.0. A map with the coordinates of localization of the sampling sites was generated using ArcGIS 9.0. Finally, the spatial modelling of Hg was done by means of kriging method (3D-Field Programme, v. 3.8.8.0, by Vladimir Galouchko, http://3dfmaps.com) as predictor tool.

3. RESULTS AND DISCUSSION

3.1. Soil Hg concentration

The level of concentration of Hg in the soil samples varied between 0.16-0.56 mg·kg^{-1}, with a mean value of 0.30 mg·kg^{-1} (median 0.30 mg·kg^{-1}). Figure 2.a shows the box-and-whisker plot showing median, mean (red square), 25th and 75th percentile levels, minimum and maximum excluding extreme values and extreme values (red asterisks) of Hg concentration in the data set. And as it can be seen in the Figure 2.b, the values of Hg concentration of two samples (*11* and *11.1*) had evidence of a different skewness (minimal) and a normal deviation around 0.10.

The concentrations obtained in this study were compared with studies carried out all over the world, such as in agricultural areas with typical anthropogenic sources from China (Zhou et al., 2018), Europe (Ottesen et al. 2013), and India (Raj et al. 2017). In general, the concentration values obtained in this study were lower or similar than the ones found in the mentioned areas. However, if the concentration values obtained in this study are compared with the ones obtained in soils around coal-fired power plants all over the world, the values found around Lacerda power plant exceed the values obtained in some areas. As it is shown in Table 1 the concentration values obtained in this study are the double than the ones obtained in soils from Spain or in Pennsylvania, in similar situations. The Hg values found in the "Four Corners" power plant from New Mexico are 10 times lower than the ones obtained in this study. The values measured around coal-power plants sited in China are the concentrations exceeding the Hg content found in the area under study.

The Hg values had also been compared with the Legislation and Guidelines on maximum Hg concentrations allow in soil of different countries such as United Kingdom (1.0-20 mg·kg^{-1} for gardens, parks, and residential areas, based on effects on human health), China (0.30-1.0 mg kg^{-1} for agricultural soil), Canada (0.80 mg·kg^{-1} for agriculture), Netherlands (reference range of 0.5-10 mg·kg^{-1}), Germany (0.10-1.0 mg·kg^{-1} based on background values), Tanzania (2.0 mg·kg^{-1} for agricultural soil), Australia (1.0 mg·kg^{-1} for agricultural soil), New Zealand (200 mg·kg^{-1} for agricultural soil), and USA (1.0 mg·kg^{-1} for agricultural soil), showing that none value exceeds the reference values (Inácio et al. 1998; CME, 2009; EPMC, 2015; EEA, 2007; TMS, 2007; EPAA, 2012; NZME, 2012; US EPA, 2002).

The sampling points with more Hg concentrations were *11*, *11.1* and *13*. Sample *11* is on one of the old deposits of fly ash and it is very close to Capivari de Baixo. Sample *13* was collected near of Tubarão and of fields of cow grass. The three points are located near to the thermoelectric plant, however, the results obtained for the soils collected geographically closer to the CFPP (see Figure 3a), indicate that the distance to the plant is not the unique factor to be considered. According to Godoya et al. (2004), the meteorological conditions at this area tend to alter Hg deposition generating air in the area as two possible diffuse Hg sources: from urban activity and from CFPP. A similar reasoning also classified the area where samples *11* and *11.1* are located as a zone with remarkable presence of heavy metals such as Sn, Fe, Pb and Tl among others (Rodriguez-Iruretagoiena et al. 2015). The sampling sites around the CFPP were *1*, *2*, *3*, *4* and *19*. Samples *2* and *3* presented higher Hg concentration values that the median value (in the range of 0.20-0.32 mg·kg^{-1}

On the other side of the river (samples *5* and *18*) presented low or similar values of Hg concentration. In the other agricultural sites near Tubarão River (*10*, *20*, *26*, *6* and *21* and *22*) the values were also lower except in a meander in the middle of the river (*26* and *6*). It can also be observed that the sampling sites located very far to the CFPP had less concentration in

comparation with the intermediates located sites. This effect was tangible in the soils from Imaruí, Treze de Maio and Imbituba.

The mean Hg concentration (0.30 mg·kg^{-1}) obtained in all sampling sites was compared to the values of Hg concentration found on each sampling sites. The sampling sites *13*, *14*, *16*, *17* and *11* are located near CFPP and between two cities, Capivari de Baixo and Tubarão and as it can be seen in the Figure 3b, these sites had higher positive values compared with the mean Hg value. Otherwise, the values of two sampling sites in Imbituba (*IMB 02* and *IMB 03* outside of the city) and in Imarui were similar to the mean Hg concentration, in contrast to *IMB01* (in the centre of Imbituba) and Treze de Maio (*TRZ1* and *TRZ2*) with lower concentration values. Considering the no anthropogenic activity on these sites, the levels of Hg concentration found on these three sampling sites (*IMB01, TRZ1, TRZ2* around of 0.17 mg·kg^{-1}) were considered as background level of Hg in the soils of the Santa Catarine state.

Whereas the Hg found in samples could correspond partially or totally, to the original (natural) composition of soils of the area, contamination factors (CFs) were calculated. These indexes compare the current Hg concentration of the soil with the pre-industrial or natural background calculated for the zone. Therefore, allows a preliminary estimation of the anthropogenic fraction in the Hg content, and provide, consequently, a common scale for inter soil comparison. According to Hakanson (1980) CF values can be broadly classified as low contamination (Class 0: CF <1), moderate contamination (Class 1: $1 \leq$ CF <3), considerable contamination (Class 2: $3 \leq$ CF $\leq$ 6) and very high contamination (Class 3: CF >6). In a first try, CFs were calculated as ratio to average Ti concentration found in the same area (the average concentration value has been obtained from the publication of Rodriguez-Iruretagoiena et. al., 2014). Since the results obtained were very optimistic, CFs were calculated using as reference or natural values: i) the lowest concentration values in the results (in our case, 0.17 mg·Kg^{-1}), and ii) the Hg reference value included in Earth Crust Tables. In the first case, the CF values for Hg ranged between 1.0-3.3, and all sampling sites showed Class 1 contamination pattern, except the sampling sites *11* and

11.1 that showed considerable contamination. Samples *4*, *13*, *16*, *17*, *22*, *28* and *35* sampling sites were classified as class 1, but their CF values were higher than 2. Although it has clear limitations, considering that they are still employed as background values for different soils around the world (Matini wet al., 2011) the values reported by Turekian and Wedepol (1961) were also used for the calculation of the CFs. The results obtained in this case were fewer optimists. More than the 60% of the samples were classified as considerable contaminated and sampling sites *11* and *11.1* presented very high contamination. The rest of the soils were moderately contaminated.

In order to dot limit the study to the 47 soils sampled Hg concentration was interpolated to unsampled sites by 3-D ordinary kriging. The kriging method is a spatial modelling that extrapolates information from discrete stations to cover the whole area of study. It is based on statistical models that include autocorrelation, that is, the statistical relationships between the measured points. The Kriging tool assumes that the distance or direction between the sample points reflects a spatial correlation that can be used to explain the variation in the surface. Consequently, the accuracy of interpolation by kriging is limited if the number of samples. In this case 2D maps of contour (isolines) on the basis of Hg numerical data was constructed using ordinary Kriging as gridding method. The contour maps are showed in Figure 4 (and Figure S1). The distribution profiles of Hg presented a rather homogeneous distribution concentration along the Tubarão river area (see Figure 4). It is remarkable that the hot spot located in Capivari de Baixo city (which includes the CFPP) has more effect in the north part than in soils located between the city and the river. This reveals that the wind plays an important role, because clearly Hg particles are arriving to soils located in the north part of Capivari de Baixo city as volatile particles as a consequence of the wind masses (northeast predominantly) and terrain orography (Possamai et al., 2010). The soils from Tubarao also presented the same distribution. The hotspots located in the south part of the river could be attributed to the intense agricultural activities carried out in the area.

In the distribution map of the coastal cities of Imaruí and Imbituba (Figure S1), the highest concentrations were found in the sampling sites located in the Imarui area, and the concentration showed a decreasing trend in direction to the centre of Imbituba city.

3.2. FE-SEM/EDS and HR-TEM/EDS analysis

Once the contamination coming from Hg was studied, to know which it was the real effect that Hg could have in living organisms and to determinate which was the bioavailability of Hg after a natural event, such as rainfalls, it was necessary to know which was the molecular structure and morphology of Hg in the soil. For this reason, soils samples with higher concentration of Hg (*11* and *13*), before and after subjected to a leaching experiment, which consist on "cleaning" few grams of soil with MilliQ water and drying, were analysed by means of FE-SEM/EDS and HR-TEM/EDS.

In the FE-SEM and HR-TEM images of the analyzed samples, different spheres were identified, as for example, spheres of Al-Fe containing Pb and As, as can be seen in Figure S2. In the mentioned figure, the spheres were coal fly ash with size between 2-5 µm, and the big bulk was the matrix of the *11* soil sample after the Milli Q water-extraction step.

HR-TEM/EDS images (Figure 5) from before or after the batch leaching process revealed the presence of carbon forms as particles or nanoparticles (CNPs) containing some potentially hazardous elements with varying degrees of crystallinity, such as multi-walled carbon nanotubes (MWNTs) encapsulating Hg, as a tendency of the Hg to complex strongly to organic carbon (Violante et al. 2008, Yang et al. 2008). Despite nanoparticles could be from natural processes, these images suggested that MWNTs were formed by the spontaneous coal combustion and were still preserved in the soil samples. The generation of CNPs created by coal-fired power station is one of the biggest problems for both human health and the environment (Ribeiro et al. 2011, Silva et al. 2011b, Liu et al. 2015, Finkelman 2004).

The iron oxides detected before and after leaching tests were spherical nanominerals of magnetite (diameter between 25–65 nm), sometimes with Hg, as can be seen in the Figure 6. Hg is more stable in the soil environment as cation (Hg^{2+}) due to its tendency to form complexes with anions or organic matter, but in our case, the major fraction appeared bound in soil minerals. Besides, it should be taken into account that this last phase could be a product of oxidation of pyrite and reactions with calcite.

In general, Hg was retained in low soluble particles such as CNPs and iron oxides, therefore, the influence of atmospheric emissions caused by the CFPP may be considered of low impact on the mobility of Hg from the soils to plants or environment in the area of studied by rain effect.

4. CONCLUSIONS

The presence of Hg found in this study, does not suppose a remarkable contamination source for the area under study. In fact, the concentration values obtained fulfil the Legislation and Guidelines currently in force for soils in different countries and were only exceeded in soils around CFPPs from China.

The anthropogenic Hg observed in the area under study does not have a unique origin. Apart from The power plant Complex Jorge Lacerda (PPCJL) the cities of Capivari de Baixo and Tubarão are important Hg sources in the area.

The leaching experiment carried out, together with the use of non-destructive analytical techniques, conclude the presence of Hg bound to CNPs or to nanominerals of magnetite, as low soluble particles, contributed to Hg retention, thus reducing the mobility of it to the waters or plants present in the agricultural area.

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Figure 1. Location of the soil sampling sites included in the study (Santa Catarina state, Brazil). The thermoelectric plant is near sampling site *1*.

Figure 2. a) Box and whisker plot of the Hg concentration data set (the lower whisker represents the bottom 25% of scores, the box represents the middle 50% of scores and the upper whisker the top 25% of scores, the line across the box shows the median score, in red asterisks represent the extreme values for the data set) and b) normal probability plot of the data set vs normal deviation, in the soil samples of Santa Catarina state.

Figure 3. a) Concentration ($mg \cdot kg^{-1}$) of Hg in the soils samples, and b) difference of concentration with the mean value in $mg \cdot kg^{-1}$ in the analyzed soil samples.

Figure 4. Spatial distribution (interpolation method: kriging) of Hg ($mg \cdot kg^{-1}$) of soils with sampling locations from the area of Tubarão–Capivari de Baixo–Jaguaruna in Santa Catarina state (Brazil).

Figure 5. HR-TEM image with an amplification of the TEM image and the EDS spectra of the darker area of the *13* sample with the presence of volatile elements like As and Hg after the leaching test.

Figure 6. HR-TEM/EDS results of the *13* soil sample: a) TEM image of some spheres (diameter between 25–65 nm) containing magnetite before leaching test, b) TEM image of two spheres with Hg before the leaching and c) TEM image of a sphere with Hg after the leaching test.

Figure S1. Spatial distribution (interpolation method: kriging) of Hg ($mg \cdot kg^{-1}$) of soils with sampling locations from the area of Imbituba–Imarui in Santa Catarina state (Brazil).

Figure S2. FE-SEM/EDS results of *11* sample with a Al-Fe-sphere containing Pb and As after leaching test with MilliQ water.