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Mercury Contamination of Soil as the Result of Long-Term Phosphate Fertilizer Production

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Abstract This study was aimed at determining the range and spatial distribution of mercury in a geographical area influenced by the emissions of phosphate fertilizers industries in Rio Grande, Brazil. The case study demonstrated that mercury concentrations in a fine fraction of the surface soil close to the fertilizer factory reached levels as high as 800 μg kg^{-1}. Increased mercury concentrations were detected up to 60 cm below the soil surface. Further, a significant impact of the elevated mercury levels was manifested in a 1-km zone around the factory. Technical grade sulfuric acid employed in superphosphate production is considered the principal source of this mercury contamination.

Keywords Fertilizer production · Mercury · Soil contamination · Sulfuric acid

A variety of human activities lead to environmental contamination by mercury. These include the pharmaceutical, paper, electric, and chemical industries (Zhang and Wong 2007), coal combustion and waste incineration (Seigneur et al. 2004), mercury and gold extractions, smelters (Castilhos et al. 1998; Gemici and Tarcan 2007), medical institutions, agriculture, and forestry practices (Porvari et al. 2003; Hylander et al. 2006; Bash and Miller 2007). The manufacture of phosphorus fertilizers is rarely included in the list of possible sources of environmental mercury contamination (Mortvedt 1996), as arsenic, cadmium, fluorine, chromium, and uranium are considered the principal pollutants of this industry (Sharma and Pervez 2004). These elements are contained in the phosphate ore in quantities exceeding their average content in the earth's crust (McClean 1980). There exist, however, data detailing the elevated concentration of mercury in some phosphate rocks (Jackson et al. 1986) that could directly result in pollution by mercury by phosphate fertilizer manufacturers using such ores. Aside from phosphate ore, other chemical components are involved in the technological production process, and they can serve as additional sources of pollution depending on the levels of mercury present. Data, however, on mercury distribution in the land immediately around phosphate fertilizer plants are absent.

A phosphate fertilizer factory in Rio Grande, Brazil has existed for more than 40 years and is one of the largest producers of phosphate fertilizer in Brazil. Previous studies in the area around the factory have determined environmental levels of pollutants such as arsenic, cadmium and fluorine (Mirlean and Roisenberg 2006, 2007). Interestingly, the pilot analyses of some soil samples showed relatively high concentrations of mercury and suggested that additional detailed research was warranted. The aim of the study, detailed herein was to determine concentrations and spatial distributions of mercury in soil that impacts the factory and, furthermore, to ascertain a source for this mercury.

Materials and Methods

The phosphate fertilizer factories under study in Rio Grande are located on a peninsula adjacent to the Patos Lagoon

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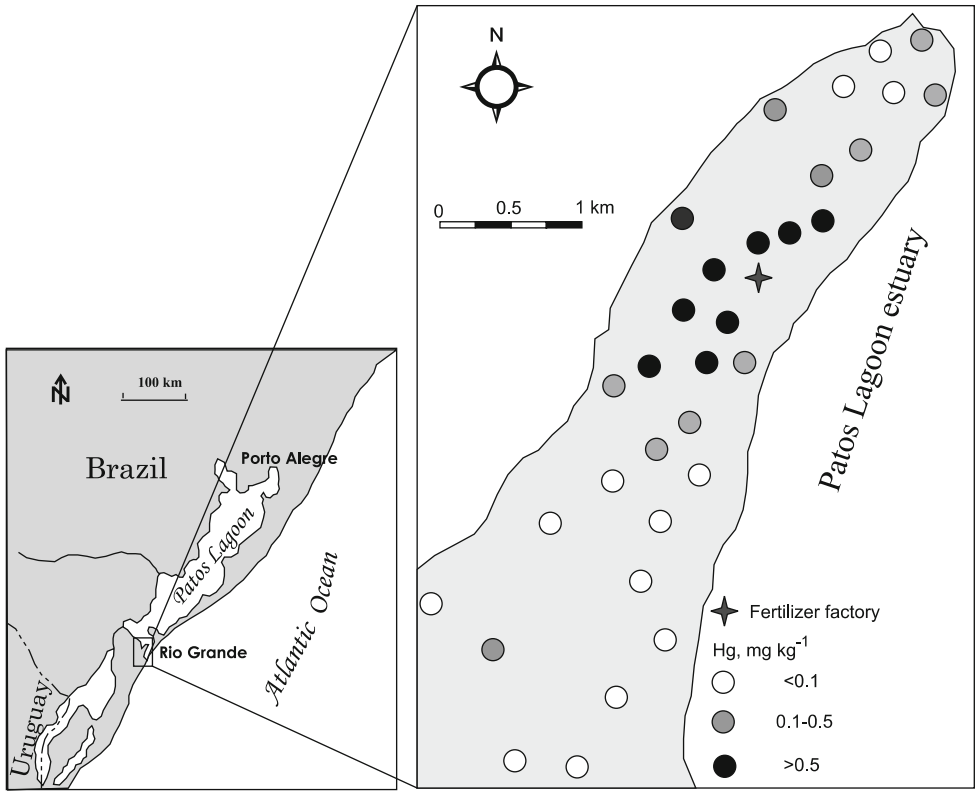

Fig. 1 Study area and point symbol map of the spatial distribution of total mercury in surface soil (fraction <63 μm)

estuary (Fig. 1). This area is characterized by a flat relief with a ridge of low dunes along the ocean coastal line. The soils of the peninsula are composed of fine-grained sand. Near the fertilizer factory is a port and two rural settlements.

Thirty-two surface soil samples (0–5 cm) were collected in the area surrounding the fertilizer factories (Fig. 1). Three additional surface soil samples were collected in remote areas (80 km from the factory), presumed to be free of industrial mercury emissions. At four points (0.5, 1.5, 3.0 and 80 km from the factory), manual auger drilling to a depth of 100 cm was carried out. Soil profiles were sampled at four depth intervals (0–5, 5–20, 20–60, and 60–100 cm). The soil samples were collected by plastic shovels and placed in polyethylene bags. Samples of the original material (natural raw phosphorites), factory products (phosphate fertilizers), and factory sulphuric acid were obtained from the local fertilizer producer.

Prior to analysis, all soil samples were air-dried at 25°C, and each sample was divided into two sub-samples that were sieved through a 2-mm and a 0.063-mm nylon sieve. The two sieve fractions (total fraction at <2 mm and fine fraction <63 μm) were separated for analyses. Finally, the soil, raw phosphorites, and fertilizer product samples were powdered with an agate mortar and pestle.

The digestion of homogenized samples was carried out according to EPA method 7471 (USEPA 1986). Samples of 0.5 g were transferred to a 100-mL volumetric flask. After the addition of 15 mL "aqua regia", the mixture was heated for 2 min in a water bath at 95°C. The flask was cooled to room temperature, and 15 mL of 5% (w/v) potassium permanganate solution was added slowly with gentle stirring. Next, the flask was again placed in a water bath for 30 min at 95°C. After cooling to room temperature, 6 mL of 24% sodium chloride–hydroxylamine sulfate (1:1, w/v) solution was added to reduce the excess permanganate. The final suspension was filtered, and the volume of the filtrate was increased to 100 mL with Milli-Q water.

Total mercury levels were measured using a cold vapor system coupled with an atomic absorption spectrophotometer (GBC 932AA). Each sample was analyzed three times, and the mean value was calculated. Maximum values of relative standard deviation (RSD) of individual samples were less than 4%. The accuracy of all analyses was ensured by sequential digestion and analysis of Certified Reference Materials of sediments PACS-2 and MESS-3 (National Research Council of Canada). Results obtained from these analyses were in agreement (±5%) with the certified values. The total organic carbon (TOC) concentration in the soils was determined using the standard method of wet oxidation (APHA 1998).

Results and Discussion

The background concentration of mercury in the topsoil horizon of the local sandy soil of total and fine fractions

was 8 ± 2 μg kg^{-1} and 25 ± 6 μg kg^{-1}, respectively. In the industrial zone the concentration of mercury in surface soil horizon varied from 28 ± 6 to 807 ± 24 μg kg^{-1} in the fine fraction and from 9 ± 2 to 117 ± 5 μg kg^{-1} in the total fraction. Mercury concentrations in the fine fraction and total fraction correlated significantly ($r = 0.94$, $p < 0.001$, $N = 32$). Spatial distributions of mercury in surface soil showed a zonal configuration with the highest mercury concentration close to factory and with levels deceasing with increasing distance from the factory (Fig. 1). Within approximately 1 km of the factory, mercury concentrations decreased by up to eight and three times in the fine and total fractions, respectively (Fig. 2).

Within a distance of 1–3 km from the factory, the mercury concentration in both fractions was 2–3 times higher than local background levels. At a distance greater than 3 km from the factory, mercury concentrations in both fractions returned to regional background levels. Such a mercury concentration distribution in surface soil coincides with the previously reported distribution patterns of fluorine and cadmium in the study area (Mirlean and Roisenberg 2006, 2007). The peculiarity of mercury distributions is, however, more dramatic than that for cadmium and fluorine, indicating a decrease in concentration levels in surface soil with an increasing distance from the factory.

The content of the fine fraction in the surface soil varied from 2.3% to 6.7% (average of 3.9%), and TOC levels ranged from 0.5% to 2.4% (average of 1.4%). Concentrations of mercury in surface soil did not correlate significantly with either the fine fraction percentage in soil or with the TOC content. The distribution of mercury along a vertical soil profile demonstrated the highest concentrations in topsoil horizon (0–5 cm) and pronounced decreases with increasing sample depth (Table 1).

Concentration of the mercury exceeding the background level values was traced in soil to interval depths of 20–60 cm only near (0.5 km) the factory. At a distance of approximately 1.5 km from the factory, the mercury concentration above the background level was evidenced in soil interval of 5–20 cm. At distance of 3 km from the factory the concentration of mercury above the background levels was found only in the topsoil horizon. In vertical soil profiles at the background site (80 km from the factory), mercury distributions were constant without significant accumulation in the topsoil horizon.

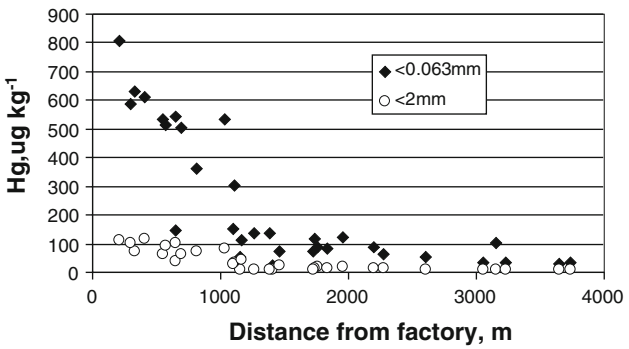

Fig. 2 Mercury concentration distributions in surface soil (fine and total fractions) versus distance from the fertilizer factory

Table 1 Vertical distribution of mercury concentrations (μg kg^{-1} ± SD) in soil profiles (fine fraction) at varying distances from the factory

Distance from factory (km)	Sampled depth intervals (cm)			
	0–5	5–20	20–60	60–100
0.5	458 ± 9	110 ± 6	43 ± 3	29 ± 3
1.5	62 ± 3	35 ± 3	21 ± 2	17 ± 2
3.0	43 ± 2	23 ± 2	21 ± 2	20 ± 3
80.0	26 ± 2	22 ± 2	20 ± 2	23 ± 2

The acidity of atmospheric fallout is the most likely factor determining the downward migration of mercury in the soil profile. A previous study (Mirlean and Roisenberg 2006) demonstrated that, at distances up to 1 km from the factory, rainwater passing through an emission plume was acidic (pH = 4.0). With increasing distance from the factory's chimney (up to 3 km), the acidity of deposits gradually decreased to pH = 6.5, explaining a deeper penetration of mercury into soil profile near the factory.

The detected high soil concentrations of mercury result from the deposition of dust and gaseous emissions on the soil surface from the factory. According to Kauwenbergh (2002), concentrations of mercury in sedimentary phosphorites vary from 55 to 400 μg kg^{-1}. Our analysis of mercury in the ore concentrate used in the factory showed similar values, ranging from 70 to 209 μg kg^{-1}, with the average of five samples calculated at 116 ± 55 μg kg^{-1}. The mercury concentrations in the final products of the factory were close to the levels in the ore concentrate, but not exceeding these values by more than two-fold, at levels of 147 ± 38, 235 ± 98 and 196 ± 65 μg kg^{-1} in superphosphate, triple superphosphate, and NPK fertilizer, respectively. Unfortunately, these data did not provide a rationalization for the accumulation of mercury (up to 800 μg kg^{-1}) in soil samples, even if the entire fine fraction consisted of fertilizer and ore particles.

The phosphate fertilizer production process involves the initial treatment of phosphate rock with sulfuric acid. The concentration of mercury in technical grade sulfuric acid can reach levels of 500 μg kg^{-1}, while the demand for superphosphate manufacture may reach as high as 2 kg per 1 kg of P_2O_5 in the ore (Angelov et al. 2002). The reaction

of sulfuric acid with phosphorite occurs at elevated temperatures (up to 80°C) and is accompanied by the release of collateral gas and vapor. A portion of the mercury contained in sulfuric acid may also be contained in these emissions. Despite the array of modern technologies employed in cleaning these emissions, a portion of by-products escapes into the atmosphere and accumulates in the environment. As the mercury is present in these emissions as a separate component, this eventually leads to mercury accumulation in the soil at concentrations exceeding those found in both the ores and fertilizers.

Our analyses of samples of sulfuric acid used in the production of superphosphate at the Rio Grande factory have displayed significant fluctuations in mercury concentrations ranging from 50 to 450 μg kg^{-1}, with an average of 247 ± 163 μg kg^{-1}. These differences are likely attributed to the origin of the sulfuric acid from different manufacturers. With a manufacturing capacity of the factory of 30,000 tons of superphosphate per month, tens to hundreds of thousands of the tons of sulfuric acid are employed annually. During the 40 year existence of the factory, hundreds of kilograms, or even several tons, of mercury have passed through the manufacturing process. Within this period, approximately 20 kg of mercury have accumulated in the topsoial horizon of soil (0 to 5 cm) in a 1-km zone around the factory. Within a 3-km zone, not more than 40 kg of mercury have accumulated in a 0–60 cm horizon of soil. This value is significantly less than that the quantity of mercury that could be historically emitted as a result of the manufacture of superphosphate. It is apparent that the primary portion of emitted mercury was dispersed in the atmosphere or removed with factory waste. The mercury accumulated in soil represents only a fraction of that washed down from emissions by atmospheric precipitations to be fixed subsequently in soil material.

The results of this study indicate that the industrial manufacture of superphosphate contaminates the environment with mercury. The most likely source of this mercury is the technical grade sulfuric acid that is used in the manufacturing process. As a constituent of industrial emissions, mercury enters the atmosphere, and a portion is deposited on the soil surface, forming contamination zones around the factory. Fortunately, the mercury concentration levels in soil determined in the current study do not exceed the permissible limits established (Inacio et al. 1998), but, when the large quantities of mercury employed in the production of superphosphate are taken into account, the level of soil contamination by mercury could be noticeably higher in other regions with older or more intense manufacturing of phosphoric fertilizers.

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References

Angelov AI, Brodski AA, Golovanov VG, Ozerov CA (2002) Line technology for simple superphosphate production. Chem Ind 11:21–26

APHA (1998) Standards methods for the examination of waters and waste waters, 20th edn. American Public Health Association, Washington DC, USA

Bash JO, Miller DR (2007) A note on elevated total gaseous mercury concentrations downwind from an agriculture field during tilling. Sci Total Environ 388:379–388. doi:10.1016/j.scitotenv.2007.07.012

Castilhos ZC, Bidone ED, Lacerda LD (1998) Increase of the background human exposure to mercury through fish consumption due to gold mining at the Tapajos river region, Para State, Amazon. Bull Environ Contam Toxicol 61:202–209. doi:10.1007/s001289900749

Gemici U, Tarcan G (2007) Assessment of the pollutants in farming soils and waters around untreated abandoned Turkonu mercury mine (Turkey). Bull Environ Contam Toxicol 79:20–24. doi:10.1007/s00128-007-9087-9

Hylander LD, Lindvall A, Gahnberg L (2006) High mercury emissions from dental clinics despite amalgam separators. Sci Total Environ 362:74–84. doi:10.1016/j.scitotenv.2005.06.008

Inacio MM, Pereira V, Pinto MS (1998) Mercury contamination in sandy soils surrounding an industrial emission source (Estarreja, Portugal). Geogerma 85:325–339

Jackson M, Hancock D, Schulz R, Talbot V, Williams D (1986) Rock phosphate – the source of mercury pollution in a marine ecosystem at Albany, Western-Australia. Mar Environ Resear 18:185–202. doi:10.1016/0141-1136(86)90032-2

Kauwenbergh SG (2002) Cadmium content of phosphate rocks and fertilizers. (Paper presented at the International Fertilizer Association Technical Conference) Chennai, India

McClean GH (1980) Mineralogy of carbonate fluorapatites. Geological Society, London

Mirlean N, Roisenberg A (2006) The effect of emissions of fertilizer production on the environment contamination by cadmium and arsenic in southern Brazil. Environ Poll 143:335–340. doi:10.1016/j.envpol.2005.11.022

Mirlean N, Roisenberg A (2007) Fluoride distribution in the environment along the gradient of a phosphate-fertilizer production emission (southern Brazil). Environ Geochem Health 29:179–187. doi:10.1007/s10653-006-9061-1

Mortvedt JJ (1996) Heavy metal contaminants in inorganic and organic fertilizers. Fertil Res 43:55–61. doi:10.1007/BF00747683

Porvari P, Verta M, Munthe J, Haapanen M (2003) Forestry practices increase mercury and methyl mercury output from boreal forest catchments. Environ Sci Techn 37:2389–2393. doi:10.1021/es0340174

Seigneur C, Vijayaraghavan K, Lohman K, Karamchandani P, Scott C (2004) Global source attribution for mercury deposition in the United States. Environ Sci Technol 38:555–569. doi:10.1021/es034109t

Sharma R, Pervez S (2004) Study of spatial variability and enrichment of selected toxic elements in ambient particulate matter around a phosphatic fertilizer plant in central India. J Sci Ind Res 63:949–956

USEPA (1986) Test methods for evaluating solid waste, vol IA, 3rd edn. National Technical Information Service, Springfield, VA, USA

Zhang L, Wong MH (2007) Environmental mercury contamination in China: sources and impacts. Environ Intern 33:108–121. doi:10.1016/j.envint.2006.06.022