



Anthropogenic mercury enrichment factors and contributions in soils of Guangdong Province, South China



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ABSTRACT

A total of 260 soil profiles were analyzed to estimate the anthropogenic contribution to total Hg content of soils in the Guangdong province by using the enrichment factor method. The results revealed that soil Manganese (Mn) as the reference element was appropriate for establishing the enrichment factor and assessing anthropogenic contribution to soil total Hg. The anthropogenic enrichment factors (EFs) suggested that some hotspots (EFs > 4) related to the anthropogenic Hg export can be identified, such as some mining of polymetallic ore in northern areas, coal exploitation in eastern areas, gold mine in western areas, and some chlor-alkali plants along the coast in the study area. The results of anthropogenic Hg contribution indicated that about 70% of the study areas suffer obvious anthropogenic Hg interference, of which anthropogenic Hg contribution to soil total Hg content was up to 72–90% in 20% of the study areas.

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1. Introduction

Mercury (Hg) as a key global pollutant has been listed as a priority pollutant by many international agencies, because of its persistence, bioaccumulation and toxicity (Jiang et al., 2006). Naturally, Hg-enriched substrate is found associated with plate tectonic boundaries, areas of high crustal heat flow, precious and base metal mineralization, recent volcanism, and organic rich sedimentary rocks (Rasmussen, 1994). The biggest anthropogenic Hg sources are fuel combustion, non-ferrous metals smelting, and industrial process of chlor-alkali plants; moreover, battery and fluorescent lamp production, cement production, and biofuel burning are also major contributors of Hg emissions (Streets et al., 2005; Wu et al., 2006; Zhang and Wong, 2007; Streets et al., 2009; Huang et al., 2011). A conservative estimate of percentage of Hg released by anthropogenic activities is approximately 50% of total Hg emission (Mason et al., 1994). The emissive Hg can come back to the earth's surface through wet and dry deposition, of which, more than 90% of it entered terrestrial ecosystem (Lindqvist et al., 1991; Fitzgerald, 1995; Matthew et al., 2005), which have caused at least a 3-fold increase in atmospheric Hg deposition to terrestrial ecosystem over the past two centuries (Schuster et al., 2002; Corbitt et al., 2011). The soil was the largest Hg acceptor. Therefore, how to identify and assess anthropogenic Hg contributions from the natural Hg level in soil is essential (Thornton, 2001).

Many studies have reported on the anthropogenic enrichment vs. natural background level of various heavy metals (Selinus and

Esbensen, 1995; Blaser et al., 2000; Rémy et al., 2003; Reimann et al., 2001, 2007). The contamination factors (CFs) or enrichment factors (EFs) were generally used as a means of identifying and estimating anthropogenic interference. Chester and Stoner (1973) or Zoller et al. (1974) defined the formula to calculate EFs to be:

$$EF_{(El)crust} = \frac{[El]_{sample}/[X]_{sample}}{[El]_{crust}/[X]_{crust}} \quad (1)$$

where "El" is the research element, "X" is the chosen reference element. The square brackets indicate concentration (such as mg kg⁻¹). Subscript "crust" represents a global average crustal concentration.

Elements Sc, Ti, Zr and Al as the reference element were widely used for calculating EFs because of their little variability of occurrence, and fractionation effects of weathering and pedogenesis. Reimann and de Caritat (2000) indicated that the approach, using the average crustal concentration as the reference could not distinguish between anthropogenic exports and natural sources because of regional variation of research elements. Blaser et al. (2000) argued that the use of parent material concentration of each individual soil profile could provide a more reasonable basis for calculating EFs than the average crust.

Generally, for obtaining meaningful EFs, the choice of reference elements must follow the below conditions (Reimann and de Caritat, 2005):

- (1) Reference element should show the low natural regional variation;
- (2) Geology factor should be the most important control on the distribution of reference element;
- (3) In natural state the ratio of a reference element to a research

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element should be little affected by natural process such as weathering.

For the first condition, the use of site-specific background value (e.g. from a deep soil layer not affected by pollution) rather than the average crust, can eliminate the natural regional variation (Blaser et al., 2000; Reimann and de Caritat, 2005). For the second condition, the regional geochemical investigation can provide the basic information; moreover, some methods of probability and statistics, such as Cumulative Distribution Function and Principal Component Analysis can be used to deal with this problem (Zhang et al., 2008). The third condition requires that the reference elements and research elements have similar transport characteristics and geochemical cycles during the pedogenic process. That means that without anthropogenic interference, the ratio of reference elements to research elements generally has a constant value; this value should be reasonable basis for calculating the EFs. And Reimann and de Caritat (2005) pointed out that for some elements such as Sc and Ti, if used as the reference elements, the ratio of the concentrations of these elements to the study elements can lead to bias in EFs calculation due to the different geochemical cycle between the reference elements and research elements. As a result, the third condition suggested us that there should be matching geochemical behavior between the reference element and research element. It means that to obtain meaningful EFs of the research element, a special corresponding reference element should be chosen according to their similar geochemical characteristics during the pedogenic process.

Moreover, Hg relative isotopic abundances were used to evaluate the contribution of the contamination source relative to the background Hg source (Estrade et al., 2011; Lefticariu et al., 2011; Feng et al., 2010; Liu et al., 2011).

In Guangdong province natural Hg sources are associated with the formation of many polymetallic ores associated with regional faults since the Cenozoic Era, such as pyrite ores, lead-zinc ores, and gold mines (GSGIO, 1993). Over the last 30 years, due to rapid urbanization and industrialization, mercury contamination have become a serious problem. Streets et al. (2005) reported that in Guangdong province anthropogenic Hg emission was up to 31.1 ton from non-ferrous metals smelting, and 7.42 ton from coal combustion, 5.72 ton from some chlore-alkali plants and other sources in 1999. Meanwhile, during 1995–2003 annual average growth rate of total anthropogenic Hg emission was 7.9%, although, coal use from the residential had been decreasing due to fuel transitions in Guangdong province, resulting in general decreases in Hg emission (Wu et al., 2006). Many large chlore-alkali plants along coastal areas also were the important anthropogenic Hg sources (SBGP, 1999). Some regional investigation for soil Hg had been carried out to reveal the spatial distribution patterns of soil Hg (Zhang et al., 2008), and pollution assessment (Chen et al., 2012). The identification anthropogenic Hg source and estimation its contribution to soil total Hg content should be of greater concern.

The aim of this paper was to identify anthropogenic Hg sources from the soil background Hg, using the soil Mn as the reference element, and quantify anthropogenic Hg contribution to soil total Hg contents on the regional scale.

2. Material and methods

2.1. Description of the study area

Guangdong Province is located in South China, between latitude 20°10′–25°31′(N) and longitude 109°41′–117°17′(E) with a total area of 1.78×10^5 km² (Fig. 1). The area has a subtropical monsoon climate with an average annual precipitation of 1336 mm and an annual average evaporation of 1100 mm. The annual average temperature is 18.7–23.4 °C with an average of 1828 hours sunshine annually. From north to south the landscape changes from mountain, plateau to flood plain. The hilly area occupies about 60% of the total area. Granite is the

most extensive parent rock of soil forming, accounting for more than 40% of Guangdong area. Larger areas of limestone and sandshale crop out in study area; and some basalt parent rock occupy in the Leizhou Peninsula (Zhang et al., 2008).

Guangdong soil profile is the typical Al-enriched weathering profile and is the product of the latest stage of weathering. It was developed on a variety of rocks, such as, granite, sandshale, limestone, and basalt. Because of the intensive eluviation and illuviation in the condition of high temperature and rainfall in the study area, the soil profiles are deficient in soluble salt, alkali metal, and alkali-earth metal, but rich in Fe and Al oxides and H⁺ (Lan et al., 2003). Therefore, the average pH value in Guangdong soil profiles is acidic in nature.

2.2. Sampling and chemical analysis

Soil samples used in this study were collected from locations shown in Fig. 1B. The sampling points in each area were selected on flat terrain. A-, B-, and C-layer soil samples were taken from 260 soil profiles at depths of 0–20, 20–40, and 40–120 cm, respectively.

Total Hg in soils was measured using the procedure by Tack et al. (2005). Approximately 0.5 g of prepared sample was weighed and placed in a 50-mL volumetric flask. Two milliliters of 1:1 HNO₃–HClO₄, 5 mL of concentrated H₂SO₄ (18 mol/L) and 1 mL of distilled water was added. After reacting for a few minutes, the suspension was heated at 230 °C for 20 min on a digester. After cooling, the digested sample was made up to 50 mL with purified water, and analyzed by cold-vapor atomic absorption spectrometry (CV-AAS) (Model PS 200 II, USA).

Total soil Mn concentrations were measured using an acid digestion method (Zhang et al., 2008). 0.2 g soil sample was digested to dryness using an acid mixture of 10 ml HF, 5 mL HClO₄, 2.5 mL HCl, and 2.5 mL HNO₃. The dry residue was then dissolved in 20% aqua regia and made up to 10 mL of solution for analysis by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) (Model PS 1000 AT, USA). The digestion process provides an effective dissolution of silicate minerals.

Forty-eight standard reference soil materials of State Environmental Protection Administration (ESS-4, Beijing, China; State Environmental Protection Administration of China, 1995) were used for QA/QC control in analyses. The results from the analyses were consistent with the reference value. The relative standard deviations were 5% (total Hg) and 2% (total Mn). The pH of soil was measured by placing 10 g of sample into 25 ml of deionized water (Chinese National Standard Agency, 1988). The soil organic matter content was measured using potassium bichromate oxidation process (Yu and Wang, 1988). Soil clay and sand contents were based on wet and dry sieving techniques and the pipette method (Gee and Bauder, 1986).

2.3. Statistical analyses

The probability and statistics of soil samples were obtained by using the software of Mintab®14.

Spatial interpolation was performed using ordinary kriging. For the low-density and background sampling, the ordinary kriging estimate can be thought of simply as an optimally weighted average of the data. It provides a best linear unbiased prediction of spatial distribution (Cressie, 1991). The spatial interpolation and contour maps displaying the spatial distribution of Hg and Mn in each layer soil were produced based on geostatistical analysis using the software of Surfer® 8.0.

2.4. Calculation for anthropogenic enrichment factor

The enrichment factor was defined to be:

$$EF_{anthro}[Hg] = \frac{[Hg]_a/[Mn]_a}{[Hg]_c/[Mn]_c} \quad (2)$$

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