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Estimations of historical atmospheric mercury concentrations from mercury refining and present-day soil concentrations of total mercury in Huancavelica, Peru

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ABSTRACT

Detailed Spanish records of cinnabar mining and mercury production during the colonial period in Huancavelica, Peru were examined to estimate historical health risks to the community from exposure to elemental mercury (Hg) vapor resulting from cinnabar refining operations. Between 1564 and 1810, nearly 17,000 metric tons of Hg were released to the atmosphere in Huancavelica from Hg production. AERMOD was used with estimated emissions and source characteristics to approximate historic atmospheric concentrations of mercury vapor. Modeled 1-hour and long-term concentrations were compared with present-day inhalation reference values for elemental Hg. Estimated 1-hour maximum concentrations for the entire community exceeded present-day occupational inhalation reference values, while some areas closest to the smelters exceeded present-day emergency response guideline levels. Estimated long-term maximum concentrations for the entire community exceeded the EPA Reference Concentration (RfC) by a factor of 30 to 100, with areas closest to the smelters exceeding the RfC by a factor of 300 to 1000. Based on the estimated historical concentrations of Hg vapor in the community, the study also measured the extent of present-day contamination throughout the community through soil sampling and analysis. Total Hg in soils sampled from 20 locations ranged from 1.75 to 698 mg/kg and three adobe brick samples ranging from 47.4 to 284 mg/kg, consistent with other sites of mercury mining and use. The results of the soil sampling indicate that the present-day population of Huancavelica is exposed to levels of mercury from legacy contamination which is currently among the highest worldwide, consequently placing them at potential risk of adverse health outcomes.

1. Introduction

1.1. Huancavelica, Peru

Colonial cinnabar mining began in Peru at the Santa Barbara Hill near Huancavelica in 1564. Colonial miners and refiners initially exported mercury to New Spain, present-day Mexico, where silver production through mercury amalgamation began in the 1550s (Cooke et al., 2009; Robins, 2011). The introduction of the amalgamation system to the Andes in the 1570s was accompanied by the imposition of the *mita* system of forced, fixed term indigenous labor. The ranks of these forced workers declined steadily throughout the colonial era as a result of metal toxicity and flight from service which left the surrounding provinces largely depopulated (Robins, 2011).

Mercury refining involved the extraction and crushing of ore, and its subsequent smelting in which the mercury was volatized, collected and ultimately shipped in liquid form to Andean silver mining centers, the most famous of which was Potosí in present-day Bolivia. Broken cinnabar ore was fired on a grate which stood approximately two to three meters off the ground in a conical roofed chamber to which it was connected to condensation tubes that passed through water on their way to a point of collection. After about four hours of combustion, draft laborers closed the air supply and were to allow the smelter to cool for about 24 h. They would then enter the

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chamber to collect the mercury on the ceiling and in the ash which had not passed through the condensation system. Despite their utility, the smelters in Huancavelica were inefficient, and mercury vapor and liquid regularly escaped from the poorly sealed joints, which was exacerbated by overheating of the ovens (Robins, 2011).

Based on colonial records of production levels of mercury in Huancavelica, an estimated 17,000 metric tons of mercury vapor escaped the smelters between 1564 and 1810, which potentially deposited in the surrounding area (Robins and Hagan, 2012). An average of 69 metric tons of mercury per year was emitted to Huancavelica's atmosphere. As a comparison, Telmer and Viega (2008) estimated that 350 metric tons of mercury is emitted globally each year from artisanal and small scale gold refining.

1.2. Health effects from mercury exposure

While individual sensitivity to mercury exposure varies, mercury poisoning may limit immune response and increase vulnerability to allergies and infections (ATSDR, 1999). Chronic elemental mercury poisoning produces physical symptoms which include tremors, pallidity, gum discoloration, loose teeth, excessive salivation, gingivitis, anemia, difficulty speaking, lack of appetite, and loss of muscular control. Such symptoms are often in concert with clinical and subclinical neuropsychological effects which may be persistent and in some cases irreversible. These include personality changes, irascibility, impatience, hypercriticism, shyness, depression, anxiety, loss of memory, obsessive–compulsive disorders, and problems concentrating and making decisions (U.S. EPA, 1997).

1.3. Comparison of global soil mercury contamination

The extent of soil mercury contamination from mining activities has been well-documented (see Table 5). Locations such as Almadén, Spain and Idrija, Slovenia were the largest mercury mines in the world, and the legacy of contamination still remains a large concern even after mining has ceased. The Santa Barbara mine near Huancavelica was another major site for mercury mining, but the distinction of this area is that much of the ore processing occurred in Huancavelica, a town that is densely populated by residents who remain largely unaware of the levels of mercury in the soil of their community.

Native soil contains both organic and inorganic species of mercury resulting from anthropogenic and natural releases into the environment, coupled with microbial and chemical activity in the soil. Because of potential human health and environmental risks, mercury is typically regulated by many government agencies. Mercury can be speciated in soil, but elemental mercury is the primary target of government regulations and management activities. All species of mercury pose a health and environmental risk, with organic species of mercury posing a greater health risk than inorganic species (Revis et al., 1990).

To our knowledge, this is the first study of widespread historical and present-day mercury contamination within the city of Huancavelica, Peru. Through use of an air dispersion model, this study aims to estimate historical health risks to the community from exposure to elemental mercury vapor resulting from cinnabar refining operations during the colonial period. Based on the estimated historical concentrations of mercury vapor in the community, the study also measured the extent of present-day contamination throughout the community through soil sampling and analysis. The results of this study will serve as the foundation for future research efforts of human exposures to historical mercury contamination in the city, particularly residential exposure.

2. Methods

2.1. Emission data

Spanish records of mercury produced in Huancavelica in 1680, a year representative of high production, were evaluated. Mercury emission rates, E_m, (in grams per mill per second) were estimated from the mercury produced in Huancavelica and registered with the colonial government using Eq. (1) for mills within the city.

$$E_m = \frac{\left(\frac{Hg_{reported}}{1-c}\right)\left(\frac{1}{1-V_1}\right) \times V_2}{n \times t} \quad (1)$$

The total mass of reported mercury production, $Hg_{reported}$, for 1680 was 594 metric tons. Taking into account widespread unregistered production (or contraband, c, which is the fraction of the total mercury produced in the mills and not reported to the government, approximately 25%) in Huancavelica, we estimated that 792 metric tons of mercury was actually produced in the city in 1680. A range of contraband has been estimated to be from 10% to 66%, depending on the time period. A thorough review of the literature provides evidence of a more reasonable range of 25% to 30% for the percentage of contraband (Robins, 2011). A volatilization fraction, V_1, of 25% was used to account for the total amount of mercury vapor released from the refining of reported and contraband cinnabar. This results in the 1056 metric tons of cinnabar ore that was available for refining at the beginning of the process. A second volatilization fraction, V_2, of 25% was used to estimate the total amount of mercury vapor released from the refining of 1056 metric tons of cinnabar ore, which equals 264 metric tons of mercury vapor. This volatilization fraction (V_2) is consistent with other values in the literature, including a recent study of 22 Chinese artisanal smelters that found a mean emission rate just under 20% (Li et al., 2008a). The total emissions were distributed equally among the number of mills in the city (n, 13 mills in 1680) and adjusted for units of time, t. This resulted in an emission rate, E_m, of 0.64 g of mercury per mill per second for 1680.

2.2. AERMOD

This study employed AERMOD, a plume dispersion and air quality model developed by the American Meteorological Society (AMS) and the United States Environmental Protection Agency (U.S. EPA). AERMOD predicts plume dispersion and ambient air concentrations at various distances from the source on the basis of source characteristics including meteorological conditions, emissions temperature, exit velocity and stack height and diameter (U.S. EPA, 2009a). AERMOD was used as a primary tool for a first approximation of the distribution of present-day soil contamination resulting from the release of mercury vapor during cinnabar refining.

AERMOD input data are usually derived from preprocessors AERMAP and AERMET. AERMAP provides geographical information, including elevation data. Although located in a mountainous region, the city of Huancavelica itself lies in a steep valley and the terrain of the valley floor is essentially flat. Considering the gentle slopes and low level emission releases, the terrain within the city is not expected to affect the concentrations; therefore, AERMAP was not utilized in this exercise. AERMET typically provides the meteorological data, which generally utilizes one to five years of hourly measured meteorological data to generate the files necessary to run AERMOD. Because long-term meteorological measurements were lacking for Huancavelica, AERMET was not used in this exercise. Instead, MAKEMET (U.S. EPA, 2010) was used to generate a matrix of meteorological conditions based on a minimum number of inputs, including ambient temperature range and land surface characteristics. AERMOD was used with MAKEMET meteorological data and the resulting air concentration estimates for the 1806 receptor