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Study on the reduction of atmospheric mercury emissions from mine waste enriched soils through native grass cover in the Mt. Amiata region of Italy

L. Fantozzi [a,*], R. Ferrara [b], F. Dini [c], L. Tamburello [d], N. Pirrone [a], F. Sprovieri [a]

[a] CNR-Institute of Atmospheric Pollution Research, c/o: UNICAL-Polifunzionale, 87036 Rende, Italy
[b] CNR-Institute of Biophysics, San Cataldo Research Area, Via G. Moruzzi 1, 56124 Pisa, Italy
[c] University of Pisa, Department of Biology, Via A. Volta 4, 56126 Pisa, Italy
[d] University of Pisa, Department of Biology, Via Derna 1, I-56126 Pisa, Italy

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ABSTRACT

Atmospheric mercury emissions from mine-waste enriched soils were measured in order to compare the mercury fluxes of bare soils with those from other soils covered by native grasses. Our research was conducted near Mt. Amiata in central Italy, an area that was one of the largest and most productive mining centers in Europe up into the 1980s. To determine in situ mercury emissions, we used a Plexiglas flux chamber connected to a portable mercury analyzer (Lumex RA-915+). This allowed us to detect, in real time, the mercury vapor in the air, and to correlate this with the meteorological parameters that we examined (solar radiation, soil temperature, and humidity). The highest mercury flux values (8000 ng m^{-2} h^{-1}) were observed on bare soils during the hours of maximum insulation, while lower values (250 ng m^{-2} h^{-1}) were observed on soils covered by native grasses. Our results indicate that two main environmental variables affect mercury emission: solar radiation intensity and soil temperature. The presence of native vegetation, which can shield soil surfaces from incident light, reduced mercury emissions, a result that we attribute to a drop in the efficiency of mercury photoreduction processes rather than to decreases in soil temperature. This finding is consistent with decreases in mercury flux values down to 3500 ng m^{-2} h^{-1}, which occurred under cloudy conditions despite high soil temperatures. Moreover, when the soil temperature was 28 °C and the vegetation was removed from the experimental site, mercury emissions increased almost four-fold. This increase occurred almost immediately after the grasses were cut, and was approximately eight-fold after 20 h. Thus, this study demonstrates that enhancing wild vegetation cover could be an inexpensive and effective approach in fostering a natural, self-renewing reduction of mercury emissions from mercury-contaminated soils.

1. Introduction

Among heavy metals, mercury is the most toxic because both inorganic and organic Hg compounds (MeHg) may accumulate in living organisms by passive diffusion across the membrane (Mason et al., 1995) or by facilitated diffusion transport (Watras et al., 1998). As a global pollutant, mercury presents a threat to human health and may be regarded as a global issue.

A significant aspect of the global biogeochemical cycling of mercury that is different from other metals is its volatility. The volatilization of mercury may occur at any stage in the transport process. Volatile species are produced by the chemical or biochemical reduction of Hg^{2+} to Hg^0 and by the biomethylation of mercury resulting in dimethylmercury (Kotnik et al., 2007). The main transport pathway for mercury is through the atmosphere, and thus, mercury represents a dangerous pollutant that has become widespread throughout the environment (Andersson et al., 2007; Pirrone et al., 2010).

The global biogeochemical cycling of Hg can only be fully understood once the amount of mercury released from natural sources is quantified (Schroeder and Munthe, 1998). The natural sources of mercury emissions are weathering of rocks, windblown dust, volcanic activity, geysers, thermal fluids, degassing of the earth's mantle, emanation from the oceans, transpiration and decay of vegetation, and forest fires. However, the amount of mercury released into the atmosphere from various environmental surfaces is still under debate. The global Hg cycle is also influenced by emissions from mining or heavily contaminated industrial areas and its environmental characterization in these areas is not only of interest on local scales, but also on a global scale (García-Sánchez et al., 2006). In the past decades there has been considerable

* Corresponding author. Fax: +39 098 4493215.
E-mail addresses: l.fantozzi@iia.cnr.it (L. Fantozzi), romano.ferrara@pi.ibf.cnr.it (R. Ferrara), fdiniprotisti@gmail.com (F. Dini), ltamburello@biologia.unipi.it (L. Tamburello).

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progress made in understanding mercury emissions from Hg-enriched soil (Ferrara et al., 1998; Wang et al., 2005). Previous field measurements suggest that mercury emission fluxes from Hg-enriched soil are 1–3 orders of magnitude greater than the predicted value (Lindqvist et al., 1991), highlighting that geologically, the Hg-enriched areas are important atmospheric Hg sources (Gustin et al., 2003), and that the contribution of Hg from natural soil to the atmosphere in earlier models may be underestimated.

To estimate annual mercury emissions fluxes accurately, the mechanisms and processes of mercury exchange between soil and air must be well understood under varying conditions. Both the intensity and nature of solar radiation have been suggested as determining factors in the increase in soil mercury emissions into the atmosphere (Gustin et al., 1996). However, many factors can influence Hg exchange flux between soil and air, including total mercury concentration in soil (Wang et al., 2005), soil moisture (Ericksen et al., 2006), soil temperature (Gillis and Miller, 2000; Moore and Carpi, 2005), Hg concentration in air (Wang et al., 2005), and rainfall and vegetation (Ericksen et al., 2006). Under different conditions the impact of each factor on the air/soil Hg exchange will be different, yet soil with a higher total Hg concentration is considered one of the dominant factors and ultimately has a greater potential for emitting Hg into the atmosphere (Gustin et al., 2003).

In order to understand mercury air–soil–plant exchange, Gustin et al. (2004) planted aspen trees (*Populus tremuloides*) in large gas exchange mesocosms (EcoCELLs) that contained soil with elevated mercury concentrations. The authors found that the presence of leaves, shielding soil surface from incident light, reduced mercury emissions from the enriched soil. Stamenkovic et al. (2008) found that emission rates from vegetated and litter-covered monoliths (measured using a dynamic flux chamber) were 5–10 times lower than emission rates measured from bare soil under the same conditions. Both light and temperature are known to influence Hg flux from soil. Some authors have found that light energy is the primary factor controlling mercury emissions from both naturally-enriched soils (Gustin et al., 2002) and mercury-polluted soils (Gustin et al., 2003; García-Sánchez et al., 2006), although soil temperature was found to play an important role (Gustin et al., 2002; García-Sánchez et al., 2006).

We located our study at the mining center of Abbadia San Salvatore (Mt. Amiata), one of the Europe's largest and most productive mining sites, in order to evaluate mercury emissions from areas that are highly contaminated by mining activities and roasted cinnabar deposits,.

The study site is characterized by the presence of large cinnabar deposits, a notable geochemical anomaly (Ferrara et al., 1998), and by high temperatures and intense solar radiation for many months of the year. Although a quarter of a century has passed since the mining activity came to a complete halt, mercury-rich processing residues and abandoned mine structures still constitute an environmental pollution problem. Moreover, ore residues were often used for road construction, for levelling soil depressions in large areas, and as material in the construction of buildings. These contaminated areas can reach soil mercury emission values of up to 10^4 ng m^{-2} h^{-1}, in the hottest season (Ferrara et al., 1998). In this way, emissions from mercury-enriched substrates constitute a significant long-term source to the global atmospheric mercury pool.

Completely reducing mercury emissions from large contaminated areas would be costly and ineffective, yet adopting a different approach to containing said emissions could be effective. Our study examines one approach by investigating the influence of native grass cover on mercury emissions by focusing on waste-enriched soils. We used a dynamic flux chamber connected to a real time mercury analyzer (Lumex RA-915+) to examine the influence of vegetation cover on the flux of mercury from contaminated soils, and to look for correlation with several different environmental factors.

2. Study sites and methods

2.1. Study sites

We measured mercury emissions on roasted cinnabar deposits near the Abbadia San Salvatore mine (central Italy) in an area that exhibited the lowest mercury concentrations in the soil. Spoil banks, made of waste from the roasting of cinnabar ore, resemble small hills around the mine, and they cover an area of ca. 120,000 m^2. The amount of mercury that has remained in the waste is exceptionally high (100–800 μg g^{-1}) and mercury continues to be emitted into the surrounding environment.

We began measuring mercury flux in August 2008, at two sampling points approximately 1 m apart. Vegetation cover characterized the first site, whereas the second site consisted of bare soil. These sites were selected based on an assumed homogeneity, particularly in terms of meteorological parameters. Subsequent chemical analysis revealed that mercury concentrations in the bare soil were approximately twice the amount measured at the site covered by vegetation. A third set of measurements was collected at an additional site, before and after removing the vegetation. In August 2009, we repeated the measurements in the same general area but at two different sites that exhibited similar characteristics to those from the previous sampling period in 2008 (one covered by native grass and one exposed, respectively). Table 1 presents the characteristics of the study sites and meteorological conditions. Both sampling periods were devoid of rain, and the most common types of wild vegetation found in the study sites were: *Agropyrum repens*, *Polygonum aviculare*, and *Avena sterilis*.

2.2. Field measurements

The mercury fluxes were collected by using a rectangular Plexiglas dynamic flux chamber (20 height × 20 width × 60 length, cm^3) and a portable mercury analyzer (Lumex RA-915+). The external air was drawn into the chamber using a 2 cm in diameter Plexiglas tube, whose opening was fixed at the height of the upper part of the chamber. This design prevented highly contaminated air at the soil surface from entering. Using a Teflon tube, the mercury analyzer extracted samples alternating between the external air (at the height of the upper part of the chamber) and the air inside the chamber. The instrument collected samples at a flow rate of 20 L min^{-1}, controlled by a mass-flow meter. The RA-915+ Mercury Analyzer is a portable multifunctional atomic absorption spectrometer, with a Zeeman background correction. The mercury detection limit is 2 ng m^{-3} in air.

We determined our two measurement sites (grass-covered and exposed, respectively) by installing Plexiglas frames (3 cm in height) at a soil depth of 1 cm. The flux chamber was positioned over the top of the frame. The top edge of the frame contained a 1 cm deep groove, into which the walls of the flux chamber fit, preventing entry of outside air. Hence, it was possible to move the Plexiglas flux chamber between the two sites within a short period of time.

After positioning the chamber on the surface and achieving good contact, we were able to reach a steady-state of internal mercury concentration within approximately 3 min. During the subsequent 2 min, we determined the average mercury concentration. The mercury concentration of external air was measured

Table 1
Characteristics of the study sites and meteorological conditions. Standard deviations refer to triplicate determinations.

	Hg soil ± S.D. (μg g^{-1})	Hg air (ng m^{-3})	T_{soil} (°C)	T_{air} (°C)	Wind speed (m s^{-1})	Hu_{air} (%)
2008 Bare soil	71.7 ± 3.4	7–63	14.8–38.5	13.5–30.0	0.1	25–50
2008 Vegetation covered soil	33.1 ± 0.3		12.1–29.9	13.5–30.0		25–50
2009 Bare soil	180.0 ± 6.4	5–35	17.3–32.5	17.6–31.5	0.2	65–85
2009 Vegetation covered soil	107.2 ± 5.0		19.2–30.5	17.6–31.5		65–85