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a cura del Comitato Organizzatore

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Do Volcanic Eruptions Solve Global Atmospheric Mercury Pollution?

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Besides human activities, volcanoes also introduce significant quantities of potentially harmful chemical compounds into the environment, mainly in the forms of gases and particles. High-temperature emissions from persistently degassing volcanoes are a known source of trace metal emissions to the atmosphere which may have important environmental consequences. Among these metals, mercury (Hg) is of particular interest since it is a toxic volatile metal found at elevated concentrations in remote regions of the world. The anthropogenic contribution to the global atmospheric Hg budget is now well constrained, with most recent estimates ranging from 1484 [AMAP/UNEP, 2008] to 1894 t yr^{-1} [2005/2006 inventory; Streets et al 2009]. Hg emissions from natural sources are, on the other hand, still poorly characterized, though being likely in the same range [estimates from 500 to 3000 t yr^{-1}; Nriagu 1989] of those reported for anthropogenic release.

The poorly constrained Hg speciation in volcanic emissions, and the limited number of studies so far, have hampered accurate estimation of the global Hg flux, with previous estimates ranging from as low as ~1 t yr^{-1} [Ferrara et al. 2000] to >800 t yr^{-1} [Varekamp and Buseck 1986]. Besides, historical archives such as ice-cores documented that large eruptions can release quantities of Hg similar to the present anthropogenic burden. The effects, or potential effects, of active volcanoes on the environment and on public health is an important issue, given the large number of communities and populated cities that exist and keep growing around and upon active and dormant volcanoes. Poisonous gases, and in the specific mercury, are also released continuously or semi-continuously into the environment by non-erupting volcanoes causing however regional environmental effects equally severe to the volcanic events of massive proportions.

A major uncertainty regarding the impacts of volcanic Hg is the extent to which Hg emitted from a volcano is deposited locally or transported globally. Actually, volcanogenic mercury fluxes are poorly constrained and there is an almost complete absence of data on the factors (magma composition, eruptive temperature, or volcanic gas composition) that influence its degassing rates at different volcanoes.

In order to better understand the role of volcanoes in the global mercury budget and to extend the currently limited dataset on volcanogenic Hg emissions, a number of field campaigns were carried out to evaluate Hg flux in volcanic gases by the simultaneously-determined Hg/SO_2 ratios and SO_2 flux. Measurements were made at the crater edge of a number of quiescently degassing volcanoes (Etna, Stromboli, Asama, Miyakejima, Montserrat, Ambrym, Yasur, Nyiragongo, Masaya). Emissions from open vents were investigated and concentrations of Hg elevated above usual background levels (rural areas far from emitting source, 1-2 ng m^{-3}) were detected. We found that in volcanic plume, mercury is mainly found as the relatively inert form of the gaseous elemental mercury (GEM) with concentrations ranging from 18 to 373 ng Hg m^{-3}. GEM has a long atmospheric lifetime estimated as 0.5-2 years due to its low solubility and gaseous nature, promoting long-range global transport [Nriagu 1989; Pyle and Mather, 2003]. High variability found in plume Hg concentrations depends on both volcanic (gas flux) and non-volcanic factors (extent of mixing and dilution in the vent; wind speed and direction), hence comparing the concentrations of Hg species between different volcanoes is not necessarily meaningful and it is more useful to compare Hg/SO_2 ratios. Using our determined Hg/SO_2 mass ratios in tandem with the simultaneously-determined SO_2 emission rates, we estimated that the investigated volcanoes have Hg emission rates ranging from 0.2 to 18 $t \cdot yr^{-1}$ (corresponding to a total Hg flux of ~54 $t \cdot yr^{-1}$).

The broad correlation found between GEM and $SO_{2(g)}$ concentrations suggests the rather similar degassing behaviour of the open-conduit volcanoes studied. Based on our dataset and previous works, we propose that a Hg/SO_2 plume ratio $\sim 10^{-5}$ is best-representative of gas emissions from quiescent degassing volcanoes. Using this ratio, we infer a global volcanic Hg flux from persistent degassing of ~95 $t \cdot yr^{-1}$. If representative of other volcanoes, these results suggest degassing of basaltic magma plays an important part of the global atmospheric Hg budget.

According to both these data and recent observations [Bagnato et al., 2010], volcanism thus would contribute from as little as 12 to as much as 78% of the estimated global natural Hg budget. Volcanic Hg

therefore has a greater potential for local and global environmental impact than Hg from the more prodigious but diffuse natural and anthropogenic sources. In particular, Hg released from Mt Etna degassing, the largest active volcano in Europe, represents approximately 5% of the total industrial Hg emissions in the Mediterranean area [~105 $t \cdot yr^{-}1$, Pirrone et al., 2009] and about 2% of the anthropogenic Hg supplies throughout Europe [~239 $t \cdot yr^{-1}$, EMEP 2002].

With these new estimates we critically revisit the idea that volcanic activity is a trivial contribution to the atmospheric Hg supply in the Mediterranean area. We shall re-examine the status of the global volcanic mercury emissions budget and its uncertainties, even when only considering quiescent phases of volcanic activity. Besides, large sectors of the planet (SW Pacific) are still un-explored, and thus our global Hg flux value estimated from passive degassing may constitutes a lower limit. However, Hg flux measurements in eruptive gases is a priority for future mercury research at volcanoes.

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