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Preliminary estimates of volcanic gaseous and particulate-phase mercury emissions at Mt. Etna and Vulcano Island

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Volcanic emissions constitute an important natural source for many chemical species into the atmosphere where, as well as the release of CO_2, SO_2 and halogens, they also emit prodigious quantities of toxic volatile trace elements, such as mercury. Mercury is a highly volatile, bioaccumulating toxic trace metal with a long (1 yr) atmospheric residence time, allowing it to be widely dispersed in the atmosphere[1] where it exists mainly in one of its two stable inorganic oxidation states: Hg^0 ($>$90%) and Hg(II). The latter form tends to be either dissolved into aqueous aerosol or adsorbed onto particles. Accurate estimate of anthropogenic as well as natural emission rates of mercury is essential for understanding the global biogeochemical cycle of this pollutant. Informations on speciation is critical when evaluating the fate of mercury emitted from point sources. Elemental mercury Hg^0 is easily distributed far from its sources whereas Hg(II) has a much greater tendency to be deposited close to the source. Samples from volcanic plumes and fumaroles at two active volcanic areas (Mt. Etna and Vulcano Island) in the Southern Italy were collected for mercury determination. The Hg emission rate from volcanic plumes can be assessed by scaling to spectroscopically obtained SO_2 outputs (**DOAS** technique). The estimate of an appropriate Hg/SO_2 mass ratio requires measurement of the distribution of Hg between vapour and particulate (condensed) phases; hence, simultaneous collection of both gas and particulate phases mercury was made. Measurement of particulate mercury was

accomplished using TPM minitraps [2], while vapour-phase mercury was collected on Au-traps. Determination of vapour and particulate-phase Hg in air was accomplished by using cold-vapour atomic fluorescence spectrometry (**CVAFS**). Based on data collected on the summit craters of Mt.Etna (North East and Voragine craters), using the Hg/SO_2 mean ratio value of 2,08*10^{-6} and the SO_2 mean flux of 1200 $\pm$ 161 t·d^{-1}(pers.com.), we estimated the time-averaged volcanic Hg flux to be about 1 t·y^{-1}. The mean gaseous Hg^0 plume concentration obtained was 33 ng·m^{-3}. A mean particulate Hg phase concentration of about 3,15 ng·m^{-3} was obtained at the Mt. Etna volcano. Generally, particulate Hg only constitutes a small percentage of the total atmospheric mercury, but under certain conditions, such as during explosive volcanic eruptions where large amounts of volcanic ash are ejected into the atmosphere, it may significantly contribute to the total atmospheric Hg content. It's important to stress that we collected mercury on Mt. Etna during a period of intensive passive degassing (2003-2005) of the volcano itself with a poor production of particulate matter that often plays as condensation nuclei for volcanic gaseous species. Hence we can say that these preliminary Hg flux estimates inside Mt. Etna plume, represent the minimum foreseen values. Besides, we carried out several measurements on the La Fossa crater at Vulcano Island which is in a steady state of passive degassing characterized by a strong fumarolic activity with temperatures varying about between 250 and 400˚C.We estimated the mean Hg emission rate from Vulcano Island fumaroles (F0 and F11 fumaroles) to be in the order of 0,012 t·y^{-1} with a mean gaseous Hg^0 concentration of about 28 ng·m^{-3}, based on a Hg/SO_2 mean mass ratio of 1,8*10^{-6} and an SO_2mean flux of 18 $\pm$ 3 t·d^{-1}.

Keywords: mercury, particulate mercury, volcanic emissions.

References: [1] Linqvist,O, Johansson, K., Aastrup, M, Andersson, A.,Bringmark, l.,Hovsenius, G., Hakanson, L.,Iverfeldt, A., Meili, M., Timm, B., 1991:*Water, Air and Soil Pollution 55,1-261*. [2] Julia Lu et al., 1998: *Analytical Chemistry, 70, 2403-2408.*