

GASEOUS MERCURY (Hg⁰) IN THE FORMER MINING AREA OF ABBADIA SAN SALVATORE (Mt. AMIATA, SIENA) AND IN QUIESCENT AND ACTIVE VOLCANIC AREAS: DISTRIBUTION IN AIR AND COMPARISON WITH OTHER ATMOSPHERIC POLLUTANTS

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INTRODUCTION

The elemental form of gaseous mercury (Hg⁰) represents a pollutant of global concern, since it is highly volatile, easily mobilized and with a residence time in the atmosphere of about one year (Schroeder & Munthe, 1998). This species is released (i) from anthropogenic sources, such as ex-mining areas or the combustion of fossil fuels, and (ii) from natural sources (*e.g.* Fitzgerald & Lamborg, 2007). In the latter case, the hydrothermal and volcanic areas play a crucial role in the emission of gaseous mercury on a global level. The World Health Organization (WHO) proposed the annual average value of 1,000 ng/m³ as a guideline for inorganic mercury in air (WHO, 2000).

With the aim to improve the knowledge on the geochemical behavior and dispersion in the air of gaseous mercury, several campaigns were conducted at both Mt. Amiata volcano (Central Italy), where a world-class Hg ex-mining district and a presently-exploited geothermal field for the production of electrical energy occur, and in quiescent and active volcanic areas, known to be important sources of this contaminant in the atmosphere despite their peculiar gaseous emissions. In particular, the ex-mining area of Abbadia San Salvatore (Mt. Amiata) was dedicated to the extraction of cinnabar until 1976 and is located in the immediate vicinity of the urban center of the same town. The facilities and the surroundings of the former mining buildings are still a source of Hg pollution (Vaselli *et al.*, 2013). The Solfatara crater (Campania, Italy), Mt. Etna volcano and Vulcano island (Sicily, Italy), Grotte Santo Stefano (Lazio, Italy) and Santorini and Nisyros islands (Greece) were selected as representative of volcanic and hydrothermal environment.

Measurements of H₂S and SO₂ concentrations were coupled with those of Hg⁰, in order to compare their behavior and to characterize in detail the emission sources. Hydrogen sulfide (H₂S), the third-most-prevalent gas species (with SO₂) emitted from active volcanic/geothermal systems after H₂O and CO₂ (D'Alessandro *et al.*, 2013), is a weakly acidic and extremely toxic gas and is immediately detectable at very low concentrations (~5 ppb) due to its distinctive rotten eggs odor. Recommended H₂S guideline value is 150 µg/m³ (~107 ppb) on 24 hours (WHO, 2000). Sulphur dioxide (SO₂), a gas with a pungent acid odor, is released in large amounts by open conduit volcanoes (*e.g.* D'Alessandro *et al.*, 2013, and references therein) and by thermal plants, industrial processes and traffic. Guidelines values are 500 µg/m³ (~190 ppb) on 10 minutes, and 20 µg/m³ (~7 ppb) on 24-hour (WHO, 2000, 2006).

The purpose of this study was to compare analytical methods and data in different environments and to estimate the impact of air pollutants in areas characterized by natural and anthropogenic sources.

MATERIALS AND METHODS

Measurement of Hg⁰ concentration in air

The determination of contaminant concentrations in air is often performed via passive/diffusive sampler techniques, such as Au-traps for mercury (*e.g.* Ferrara *et al.*, 1994) or radial-type (Radiello[®]) passive samplers for H₂S (*e.g.* D'Alessandro *et al.*, 2013), which exclude the instantaneous monitoring of the contaminant distribution in the air, since they retrieve cumulate concentrations based on the exposure time.

The use of a portable instrument dedicated to continuous measurements of gaseous elemental mercury (Lumex[®] RA-915M; Sholupov *et al.*, 2004, and references therein) (Fig. 1a), based on atomic absorption spectrometric technique with Zeeman effect, allowed to execute real-time, immediately viewable and high frequency measurements of Hg⁰ concentration. The detection limit of Lumex is 2 ng/m³ at a flow rate of 10 L/min, the accuracy is 20% and the dynamic range covers four orders of magnitude (2-50,000 ng/m³). The measurement campaigns with Lumex were carried out by:

1. pathways within contaminated areas, covered using a car or on foot;
2. measurements at fixed points, recording Hg⁰ variations for a predetermined period.

Combined measurements of Hg⁰ and H₂S-SO₂

The measurements of gaseous mercury were coupled with those of H₂S and SO₂. The latter were carried out using i) Thermo[®] 450i, and ii) Multi-GAS (Fig. 1b,c). Thermo[®] 450i uses pulsed fluorescence to measure the concentrations of SO₂, whereas H₂S is measured as SO₂ after oxidation. The detection limit of this instrument is 1 ppb at a sample flow rate of 1 L/min, the precision is 1%, whereas the dynamic range is from 0-0.05 to 10 ppm. The Multi-GAS (Multi-sensor Gas Analyzer System, INGV-Palermo; Aiuppa *et al.*, 2009, and references therein) is able to measure in real-time concentrations of SO₂, H₂S or other species such as CO₂ depending on the specific installed electrochemical sensor. The SO₂ and H₂S sensors are characterized, respectively, by a calibration interval of 0-200 and 0-50 ppmv, precision of 2% and detection limit of 0.5 and 0.05 ppmv at a flow rate of 0.6 L/min.



Fig. 1 - The Lumex[®] (a), Thermo[®] (b) and Multi-GAS (c) instruments.

The combined measurement technique requires the synchronization of the two instruments (Lumex + Thermo or Lumex + Multi-GAS) and the simultaneous acquisition of coincident high frequency data. Measurements were carried out along pathways (up to 12 km long) at an average speed < 10 km/h and coupled with GPS data and meteorological parameters, such as air temperature, humidity, wind intensity and speed. By processing the acquired data, distribution maps of each contaminant were constructed.

Measurement of Hg⁰ fluxes from soil

Measurement tests of Hg⁰ fluxes from soil were carried out by using an accumulation chamber placed onto the ground and directly connected to the Lumex in order to have a closed circuit system as the sampled gas was re-injected into the chamber. The soil gas was continuously pumped from the chamber and conveyed to the Lumex by means of plastic tubes. By the data processing, the α coefficient was determined. This coefficient represents the increase of the initial portion of the concentration vs. time straight line and is the key parameter to calculate the flux similarly to what proposed for the CO₂ fluxes (Chiodini *et al.*, 1998). Nevertheless, the absence of an appropriate calibration, the great variability of Hg⁰ concentrations and the almost never uniform increase of the concentration vs. time did not allow to calculate a realistic diffuse Hg⁰ flux. To overcome these uncertainties, specific laboratory tests were carried out at the University of Palermo, in order to approach a different methodology based on the principle of static chamber. We initially proceeded to the Lumex calibration. The calibration curve was built by injecting different volumes of Hg-saturated air into the Lumex inlet. Each new aliquot produced a peak, which had an area proportional to the air volume, which in turn was proportional to the

amount of the injected Hg^0 (Fig. 2a). The relationship between the different amounts of injected Hg^0 and the respective calculated areas under the corresponding peaks allowed to draw the calibration curve (Fig. 2b).

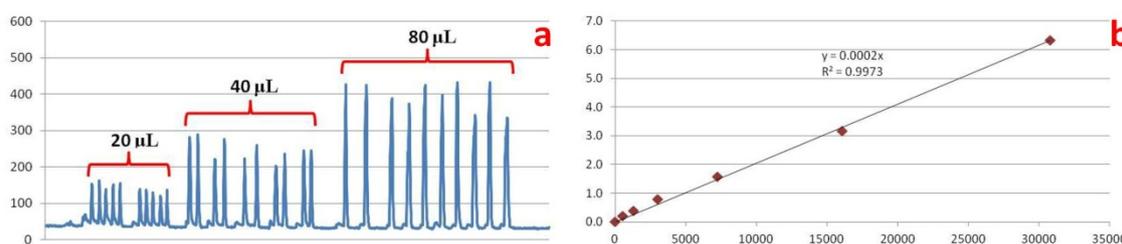


Fig. 2 - Graphical representation of 3 sets of 10 injections at different volume (20, 40 and 80 μL) performed during the calibration phase (a), and the calibration curve (in x-axis the peak area, in y-axis the amount of injected Hg^0) (b).

The discrete injections method can be a useful tool for the direct measurement of diffuse Hg^0 soil flux. A general procedure to calculate the Hg^0 flux from soils can be summarized, as follows:

1. positioning a static chamber, equipped with a porous septum penetrable with a syringe, onto the soil;
2. sampling of a predefined volume of the soil gas accumulated inside the static chamber, at predetermined intervals of time with a syringe;
3. injecting each sampled gas aliquot from the static chamber into the Lumex inlet to measure the Hg^0 concentration;
4. estimating the Hg^0 flux by calculating the amount of the injected Hg , to be related to the time increase and static chamber geometry, as a function of calibration curve produced in laboratory.

Measurement of Hg^0 concentration in hot wells

In order to verify the release of gaseous mercury from wells water surfaces characterized by a thermal anomaly, a method was developed using Lumex. The measurement was carried out by connecting Lumex to a tube of plastic material (Rilsan[®]) with constant section (6 mm diameter) through a 3-way stopcock. In order to reach the desired depth and to ensure the vertical position, a weight was placed at the lower end of the tube. Lumex was set to high frequency acquisition, in order to verify, in real-time, the changes of Hg^0 concentration and to evaluate possible “stratifications”, produced by air masses presenting Hg^0 increments.

Moss-bags

Mosses, for their unique morphological and physiological characteristics, have the ability to accumulate large quantities of trace metals by both dry and wet deposition and are therefore useful to recognize their sources of pollution (Calabrese *et al.*, 2014, and references therein). Sphagnum moss from an uncontaminated Swedish area and characterized by excellent water retention, surface wettability and cation exchange capacity (Calabrese *et al.*, 2014) was used. The mosses were repeatedly washed and dried at room temperature. About 2 g of moss were then packed in nylon bags to form a sphere of about 5 cm in diameter. Once in the field, at each measurement site, a 2 m high wooden stick was fixed into the ground at which an uncovered and covered (with a plastic protection) moss was attached to evaluate the different impact of dry and wet deposition, respectively. Hg^0 concentrations were also measured by Lumex.

In the lab, the mosses were dried at 40 °C for 48 hours, weighed and powdered with an agate mortar. The powdered mosses were subsequently dried at 40 °C for 24 hours. The analysis of mercury (Hg_{tot}) was then performed using atomic absorption spectrometric technique with an Hydra C instrument (INGV-Palermo).

(09/2012), Nisyros crater (06/2013), Solfatara di Pozzuoli crater (09/2013-04/2014), Mt. Amiata geothermal field (06/2014) and Vulcano (09/2014).

The average Hg^0 concentrations in the diluted plume of Etna at Torre del Filosofo amounted to 15 ng/m^3 . The maximum Hg^0 concentration (75 ng/m^3) was much lower than the values measured on the crater rim ($200\text{--}300 \text{ ng/m}^3$, Bagnato *et al.*, 2007), indicating an evident dilution process taking place because of the intensity of the prevailing winds. In contrast, the minimum value (4 ng/m^3) measured outside the plume was consistent with the natural background values (3 ng/m^3 ; Bagnato *et al.*, 2007). The SO_2 concentrations (measured with Multi-GAS) varied between 0.2 and 3 ppm, exceeding the guideline values suggested by WHO (2000, 2006). Comparing Hg^0 concentration trends with those of SO_2 , correspondences were found, confirming that the anomaly of gaseous mercury was directly linked to the diluted plume.

Measurements within the Nisyros caldera were carried out through transect walk and included the fumarolic areas of Stefanos and Kaminakia craters and Lofos dome. The maximum Hg^0 concentration was 493 ng/m^3 (Kaminakia), whereas the minimum values were consistent with the natural background measured outside the caldera rims ($< 15 \text{ ng/m}^3$). The maximum H_2S value (58 ppm, measured with Multi-GAS) was achieved approaching the Kaminakia crater. The main fumarolic emissions inside the crater were clearly highlighted by anomalously high Hg^0 concentrations ($> 100 \text{ ng/m}^3$) with respect to the surrounding air masses ($< 30 \text{ ng/m}^3$). A good match between Hg^0 and H_2S concentration peaks was achieved, while the variability in the continuous concentration trend probably depended both by the effect of the wind and the dilution of the fumarolic plumes.

The measurements inside the Solfatara were made through transects on foot inside the entire crater area. The Multi-GAS was dedicated to the measurement of H_2S concentrations. The maximum Hg^0 concentration was $9,523 \text{ ng/m}^3$, the minimum 15 ng/m^3 (consistent with 18 ng/m^3 measured outside the fumarolic area; Bagnato *et al.*, 2009). The H_2S concentrations ranged from 0.4 to 23 ppm. A good match between Hg^0 and H_2S concentration peaks was not always achieved. This was probably due to the multiple emission sites from Solfatara, which include both the fumaroles and the crater floor whose soil is characterized by the absence of vegetation due to diffuse release of hydrothermal gases (Tassi *et al.*, 2013). The highest measured Hg^0 concentrations ($> 100 \text{ ng/m}^3$) were close to the main fumarolic emissions, and in particular around Bocca Grande and Bocca Nuova. High concentrations were achieved even at the Stufe, two ancient caves covered with brick, and Fangaia, located in the central area of the crater and consisting of mud pools produced by a mixing of rain water, fumarolic fluids and clay materials (*e.g.* Tassi *et al.*, 2013, and references therein). The remaining areas were affected by emissions depending on proximity and winds trend, prevailing from SW. Outside the crater the Hg^0 values were $< 45 \text{ ng/m}^3$, probably due to the presence of vegetation altering the soil thickness, exposure to sunlight, moisture and temperature and so influencing Hg^0 release in the atmosphere (*e.g.* Gustin *et al.*, 2004).

On 16 and 17 April 2014, pathways (by car) with combined Hg^0 and H_2S (Thermo) measurements were performed within the Solfatara crater. The maximum Hg^0 concentration was 77 ng/m^3 , the minimum 12 ng/m^3 (consistent with 18 ng/m^3 measured outside the fumarolic area; Bagnato *et al.*, 2009). The H_2S concentration varied between 0.0002 and 2.4 ppm, exceeding the H_2S guideline value suggested by WHO (2000). H_2S , despite a clear correlation, showed some inhomogeneities in the high frequency trend compared to mercury, indicating a different emission mechanism. As already highlighted by September 2013 data, the H_2S concentrations were above the typical values of clean air (from 10^{-3} to 10^{-1} ppm) in the whole area (Aiuppa *et al.*, 2013).

A whole week (23 to 29 June 2014) was dedicated to combined Hg^0 - H_2S measurements by Lumex-Thermo between the towns of Abbadia San Salvatore and Piancastagnaio (Mt. Amiata). The measurements were carried out along the same pathway repeated each days, and at fixed points. The maximum Hg^0 concentration measured in the transects was 625 ng/m^3 (exceeding 300 ng/m^3 in open air), the minimum 18 ng/m^3 (consistent with the natural background of $\sim 10 \text{ ng/m}^3$; Ferrara *et al.*, 1998). The maximum H_2S concentration measured in the transects was 1,061 ppb (> 107 ppb with an average time of 24 hours; WHO, 2000), the minimum 0.1 ppb. The distribution of Hg^0 and H_2S pointed out that the maximum concentrations occurred in the vicinity of geothermal power plants of Piancastagnaio (PC3, PC4 and PC5), reaching values $> 100 \text{ ng/m}^3$ for Hg^0 and > 25

ppb for H₂S, as expected since significant concentrations of these contaminants characterized the geothermal vapors. The plume dispersion was concordant with the wind, intercepting sometimes the town of Piancastagnaio.

On 7 to 11 September 2014 a Hg⁰-H₂S-SO₂ measuring campaign was carried out through Lumex-Thermo at Vulcano both on tracks and at fixed sites. Measurements involved areas where direct or diffuse gaseous emissions were present (Spiaggia di Levante, Forgia Vecchia, Vecchio Faraglione, Valle della Roia), although distal areas, such as Vulcanello, Gelso Porto and Capo Grillo, were investigated to evaluate the impact of gas pollutants on the whole island and to verify the presence of other sources of contaminants. The maximum Hg⁰ concentration measured in the transects varied between 14 and 22 ng/m³, the minimum between 5.4 and 11 ng/m³ (consistent with the natural background of ~4.8 ng/m³; Aiuppa *et al.*, 2007). The H₂S concentration varied between 0.1 and 392 ppb (> 107 ppb with an average time of 24 hours; WHO, 2000), whereas those of SO₂ were between 0.1 and 34 ppb (> 7 ppb on 24 hours; WHO, 2006). The gaseous mercury showed a trend without major fluctuations, with values always < 25 ng/m³ compared to a baseline of 5 to 10 ng/m³, possibly due to prior oxidative processes affecting the hydrothermal fluids (*e.g.* Varekamp & Buseck, 1984). The relationship between H₂S and SO₂ peaks testified that the latter can be produced by oxidative processes acting on the former, whereas the presence of some SO₂ peaks not correlated with H₂S denoted a possible direct contribution from the volcanic summit (Fig. 4). The main factor controlling the distribution of contaminants in the air is, in addition to wind, the large number of emission sources, consisting of fumaroles, soil diffuse gases and boiling and bubbling pools.

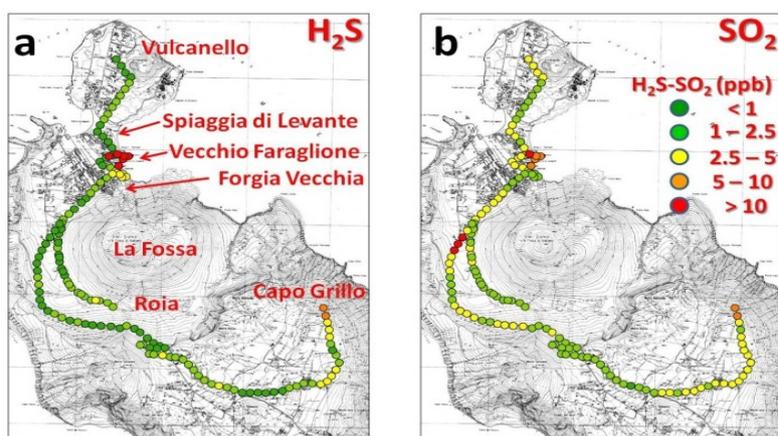


Fig. 4 - Map showing the concentrations of H₂S (a) and SO₂ (b) and the localization of the main gases emission areas.

Measurements with accumulation chamber connected to Lumex

As previously mentioned, no reliable Hg⁰ soil flux values were obtained by connecting Lumex and accumulation chamber. Consequently, for the campaigns at Vulcano (June 2012) and at the ex-mine of Abbadia San Salvatore (May 2013), the technique of the Hg⁰ maximum value measured inside the chamber was adopted.

The sampling at Vulcano was performed in the surrounding areas of Spiaggia di Levante, Vecchio Faraglione and Valle della Roia, but also Vulcanello, Gelso Porto and the inner area of Vulcano Porto. The measurements are to be considered only indicative, as the campaign was primarily designed to test the method. The highest Hg⁰ values (>50 ng/m³) were recorded between Spiaggia di Levante and Vecchio Faraglione, *i.e.* in correspondence of the main emissions fed by the underlying low temperature hydrothermal system (Capaccioni *et al.*, 2001). Valle della Roia and the sporting grounds of Vulcano Porto, known to be characterized by intense diffuse degassing, did not record anomaly, as well as at Vulcanello.

The second campaign was carried out at selected points within the former mine of Abbadia San Salvatore, in order to verify and localize possible accumulations of buried contaminated material. A wide variability of maximum concentration data detected in the chamber (by tens of ng/m³ up to > 50,000 ng/m³, *i.e.* Lumex oversaturation) was recorded. The highest concentrations mainly corresponded to those areas located in front of the furnaces buildings, where in the past carryover terrains and products from the processing of cinnabar were

placed, such as slag and/or by-products (Vaselli *et al.*, 2013). The high variability in terms of Hg^0 concentrations depended generally from the more or less high degree of contamination of all the terrains.

Measurements with the method of the peaks areas

The proposed method for calculating the diffuse Hg^0 soil fluxes, which combines a static chamber and the calculation of the amount of Hg of the concentration peaks had a first experimental phase at Solfatara (September 2013) and Grotte Santo Stefano (May 2014). In particular, tests were made via an injection in Lumex in the first campaign and through a direct measurement within foils driven in the ground in the second campaign.

At each point inside Solfatara, an aliquot of soil gas was taken and injected gradually into the Lumex. The mercury amount, proportional to the area of the corresponding concentration peak, varied in a wide range between a minimum of ~ 0.01 ng and a maximum of 19 ng. The results indicated that the highest values are found near the fumarolic area at the southeastern side of the crater and the area of the Stufe. At the same time, the lowest values corresponded to distal areas to the emissions, and to the wooded zone on the western side.

Such a measurement technique was repeated at Grotte Santo Stefano. The only difference consisted in the direct gas aspiration, via a connection tube, from the foil driven into the ground, without discrete injections. In this specific case, knowing the total aspiration time, the ng/hour of Hg emitted from each point (considered as hypothetical continuous emitter) was estimated. The mercury amount varied between a minimum of ~ 0.01 ng and a maximum of 12 ng, whereas the mercury amount vs. time varied between 15 and 218 ng/hour. A homogeneous distribution of the emissions was not found, presumably because the emission rates depended on the combination and interdependence of multiple processes. In areas with vegetation cover, processes preventing the release of gaseous mercury had the predominance, in relation to the presence of organic matter in the soil (Gustin *et al.*, 2004). In the central areas, characterized by intense soil formation and alteration, volatilization was instead probably favored.

Hg^0 measurements in hot wells

The direct measurement of the Hg^0 concentration within wells characterized by a water thermal anomaly was carried out in two separate series of measurements, conducted at Santorini (June 2012) and Vulcano (July 2012). The data continuous acquisition enabled to reconstruct the Hg^0 vertical profile in each well.

One of the most important results obtained using this approach is relative to a detailed study carried out at the Chantal well, located in the inner part of Vulcano Porto, whose waters have a temperature of 51 °C, with a depth of about 15 meters. The measurements showed that Hg^0 concentrations increase with depth, with values ranging from 9.2 to 73 ng/m³. At Santorini, Hg^0 measurements were carried out in 4 selected wells using the same method adopted at Vulcano. These wells, however, differ substantially from Chantal, as they are less deep and characterized by a less accentuated thermal anomaly. The wells analyzed did not show significant variation of the Hg^0 concentration with depth. The minimum measured value (28 ng/m³) was found at the bottom of one of the wells. We can therefore argue that the establishment of air masses having different Hg^0 contents within a well depended on the depth and, above all, on the waters temperature.

Hg measurements through moss-bags

The measurement of the mercury accumulation through moss-bags was carried out in two months in October 2013 at 10 sites in the Mt. Amiata area. Mercury accumulation in moss exposed to the atmosphere (uncovered) resulted higher than that covered, as also confirmed by higher values of the accumulation factor (obtained by dividing the median value of each moss for the median value of the blank sample), which reached a maximum of 966. This depended on the predominance of wet depositions on dry ones, even though the latter were still important transport vehicles especially where a constant and abundant Hg^0 source is present (Lodenius, 1998). The minimum and maximum Hg^0 concentrations of the covered mosses varied, respectively, between 101 and 323 ng/g and between 136 and 653 ng/g, whereas those in the uncovered mosses varied, respectively, between 209 and 54.092 ng/g and between 923 and 133.842 ng/g. The highest Hg^0 concentrations measured with

Lumex were 14,761, 18,594 and 19,927 ng/m³ and corresponded with the location of the most contaminated mosses.

CONCLUSIONS

This work focused on the study of the distribution and the geochemical behavior of gaseous elemental mercury (Hg⁰) emitted into the atmosphere by anthropogenic (*e.g.* ex-mining areas) or natural (*e.g.* volcanic areas) sources, by evaluating the measured concentrations as an indicator of air quality. The comparison between the different sources of pollution concerned also H₂S and SO₂. The method chosen to assess accurately the environmental behavior and the distribution of the contaminants was to use dedicated instruments (*e.g.* Lumex), equipped with detectors able to high frequency measurements, along pathways at a speed approximately constant, using a car or moving on foot, or by making continuous measurements from fixed points. The main conditioning factor in the transport and distribution of atmospheric gases was the wind, able to control the direction of dispersion of the plume emitted from the pollution sources. Lumex was also used to apply the method of the accumulation chamber to the measurement of Hg⁰ flux from soils. The difficulty in estimating correctly the increase in concentration highlighted the importance of instrumental calibration on gas injection into the measuring instrument, which provided the basis for flow measurements with a static chamber. A further Lumex application concerned the measure, along a vertical profile, of Hg⁰ concentrations within wells characterized by a water thermal anomaly, that allowed to verify the presence of air “stratification”. Finally, the mercury accumulation capacity of selected mosses was tested, and the results showed that the wet depositions constituted the main vehicle through which the accumulation took place, in particular on uncovered mosses.

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