

MOBILITY OF MERCURY IN THE VOLCANIC/GEOTHERMAL AREA OF NISYROS (GREECE)

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Abstract

In the summer 2013, mercury concentrations in soils and air from Nisyros (Greece), an active volcanic island located in the Aegean Sea, were determined. Up to 102 samples of soil were collected in the Lakki plain caldera and analyzed for mercury by using a cold vapour atomic absorption analyzer, following 7473 US EPA method. Concentrations of mercury in air were also investigated in the same sites with a portable spectrophotometer (Lumex RA-915M). Soil mercury concentrations were in the range from 0.023 to 13.7 µg/g. The mercury concentrations in air showed high background values in the Lakki plain caldera, ranging from 21 to 36 ng/m³ and maximum values up to 493 ng/m³ in the proximity of the fumarolic areas, in contrast with the relatively low values (from 2 to 5 ng/m³) measured in the distal sites outside of the caldera. The positive correlation between mercury and CO₂ and H₂S in the atmosphere highlights the important role of fumarolic gases as carrier for gaseous mercury (Hg⁰). On the contrary, mercury does not show significant correlations with CO₂ and H₂S in the soil gases. This finding evidences the complexity of the processes affecting mercury in hydrothermal gases passing through the soil.

Keywords: soil mercury, atmospheric mercury, hydrothermal gases, carbon dioxide, hydrogen sulphide.

Περίληψη

Το καλοκαίρι του 2013, προσδιορίστηκαν οι συγκεντρώσεις υδραργύρου στο έδαφος και τον αέρα του ενεργού ηφαιστείου της Νισύρου (Ελλάδα), το οποίο ανήκει στο ενεργό ηφαιστειακό τόξο του νοτίου Αιγαίου. 102 δείγματα εδάφους συλλέχθηκαν και

αναλύθηκαν για υδράργυρο με τη χρήση ψυχρού ατμού ατομικής απορρόφησης αναλυτή, σύμφωνα με τη μέθοδο EPA 7473. Ταυτόχρονα, στα ίδια σημεία πραγματοποιήθηκαν συγκεντρώσεις υδραργύρου στον αέρα, με φορητό φασματοφωτόμετρο (Lumex RA-915M). Οι τιμές των εδαφικών συγκεντρώσεων υδραργύρου κυμαίνονται από 0.023 έως 13.7 mg/g. Οι συγκεντρώσεις υδραργύρου στον αέρα έδειξαν υψηλότερες τιμές υποβάθρου στην περιοχή Λακκί της καλδέρας, μεταξύ 21 και 36 ng/m³ και μέγιστες τιμές μεγαλύτερες από 493 ng/m³ κοντά στις φουμαρολικές περιοχές, σε αντίθεση με τις σχετικά χαμηλότερες τιμές (από 2 μέχρι 5 ng/m³) που μετρήθηκαν σε σημεία μακριά από την Καλδέρα. Η θετική συσχέτιση μεταξύ υδραργύρου, διοξειδίου του άνθρακα και υδροθείου στην ατμόσφαιρα υποδηλώνει το σημαντικό ρόλο των φουμαρολικών αερίων ως φορείς αερίου υδραργύρου (Hg⁰). Αντίθετα ο υδράργυρος δεν παρουσιάζει σημαντική συσχέτιση με το CO₂ και H₂S των εδαφικών αερίων δειγμάτων. Αυτό το συμπέρασμα υποδηλώνει την πολυπλοκότητα των διαδικασιών που επηρεάζει τον υδράργυρο που βρίσκεται στα υδροθερμικά αέρια εντός του εδάφους.
Λέξεις κλειδιά: εδαφικός υδράργυρος, ατμοσφαιρικός υδράργυρος, υδροθερμικά αέρια, διοξείδιο του άνθρακα, υδροθείο.

1. Introduction

Volcanoes and geothermal areas are natural sources of compounds that are potentially dangerous for the environment and for the human health. High amounts of gases such as of CO₂, H₂S, SO₂, HF and other including gaseous mercury (Hg⁰), are emitted both actively and due to the passive degassing. Trace metals were found at significant concentrations in hydrothermal fluids, being associated with uprising gases. Trace metals even if in very low amount have a significant impact on the biosphere, atmosphere and hydrosphere.

Among the volcanic trace volatile elements, mercury (Hg) is one of the most environmentally-significant (Mason *et al.*, 1994) because of its extreme mobility and toxicity (Lamborg *et al.*, 2003). The biogeochemistry of Hg is a highly complex issue due to the exchanges between atmospheric, terrestrial and marine pools (Fitzgerald *et al.*, 1991). These exchanges are mainly driven by microbial activity, dark abiotic and photochemical reactions affecting the Hg speciation and bioaccumulation (Morel *et al.*, 1998). Mercury is emitted in several forms: elemental (metallic) mercury, inorganic mercury compounds, and organic mercury compounds. Metallic mercury (Hg⁰) is highly volatile due to its high vapour pressure that permits a long-range transport in the air. Monovalent and divalent mercury are soluble in the water; the divalent mercury, Hg(II), is more stable than monovalent Hg(I), and common in the environment, it may undergo complexation, precipitation with inorganic ligands, and sorption onto the soil matrix. The toxicological properties of mercury for environment and human health depend on the physical and chemical form in which it occurs. Hg vapors, for example, are very dangerous if inhaled, due to their ability to reach the lungs causing pulmonary edema, pain and peeling of the respiratory epithelium of the bronchi.

Mercury, as constituent of volcanic and geothermal fluid (Barnes and Seward, 1997; Bagnato *et al.*, 2007), is discharged in the water and released into the atmosphere as Hg⁰ being in association with the reducing non-condensable gases (Nimik *et al.*, 2013; Robertson *et al.*, 1977).

Since in the last decades, authors underlined the correlation in hydrothermal fluid discharged between mercury and hydrogen sulphide (e.g. Vitolo and Saggiani, 2002) related to the formation of solid HgS. Hydrogen sulphide is an odorous pollutant and it is commonly regarded as toxic; it is corrosive and poses severe concerns for human health.

Nisyros Island is a quiescent volcano emitting hydrothermal gases from fumaroles and through soil degassing. Its hydrothermal fluids are particularly rich in H₂S, causing a low pH on soils they permeate (Daskalopoulou *et al.*, 2014). The main aim of this work is to calculate the Hg emitted from the hydrothermal area of Nisyros (Greece) in its gaseous form and measure the concentrations

of this pollutant in the soil. These results were compared with H₂S and CO₂ data measured in soil gases and in the air.

2. Study area

Nisyros Island is a quiescent volcano located in the easternmost volcanic group of the South Aegean active volcanic arc. The volcanic edifice developed in the last 200 ka through five distinguished stages (Hunziker and Marini, 2005) that led to the formation of a caldera about 4 km in diameter. The most recent activity is represented by hydrothermal explosions forming several phreatic craters, the last of which occurred in 1887 (Hunziker and Marini, 2005). The Lakki Plain represents the south-eastern remnants of the calderic depression after the emplacement of a series of volcanic domes filling up the north-western part. Fumarolic fields are currently present in this area, mainly within the hydrothermal craters strongly controlled by fracturing along the main NW- and NE-trending active fault systems (Papadopoulos *et al.*, 1998) and are fed by a >1000 m deep hydrothermal system having a temperature of 300-350°C. The fumarolized hydrothermal craters can be subdivided into three main groups: The oldest one comprises the Kaminakia craters, the second consists of the Stephanos crater, whereas the third one corresponds to the youngest area where a post-calderic dome (Lophos) is placed and includes the Phlegeton, Polybotes Megalos and Polybotes Micros craters (Caliro *et al.*, 2005; D'Alessandro *et al.*, 2013). Water vapour (91-99%) is the main component of the fumarolic fluids, followed by CO₂ and H₂S. The estimated total output of CO₂ and H₂S is close to 1 kg/s and <0.3 kg/s, respectively (Caliro *et al.*, 2005; D'Alessandro *et al.*, 2013).

3. Materials and Methods

A multidisciplinary field campaign was carried out on June 2013 at Lakki Plain, Nisyros Island, where soil gases and soils were sampled and Hg⁰, H₂S and CO₂ in the air were measured. A total of 102 soil gas samples were collected at Lakki plain mostly in the fumarolic areas of Kaminakia, Stephanos, Micro Polibotes and Phlegeton craters, and in the areas of Ramos and Lophos (Fig. 1).

Gases were sampled at 50 cm depth using a Teflon tube of 5 mm ID equipped with a tight plastic syringe to avoid air contamination. The over-pressured vials were used for H₂S and CO₂ analysis by using Micro Gas Chromatography with a Micro GC MSHA CP-4900 having 3 independent modules.

Ground temperature was measured at 20 cm depth by using thermal probes and a digital thermometer; these measurements were carried out 10-15 min after the insertion of the thermal probe in the soil in order to achieve thermal equilibrium.

Soils were collected from the first 3 cm of depth at 119 spots at Lakki Plain. Soil samples were homogenized and powdered. Homogenized samples were used for the analysis of total Hg, performed using a DMA-80 analyzer (an atomic absorption spectrophotometer, Milestone, Wesleyan University, Middletown, CT, USA). About 10 mg of dry soil were loaded into specific nickel boats and analyzed according to the US-EPA 7473 method. Accuracy was checked by running replicates of the reference materials NCSDC7701 (0.015±0.006 mg/kg) and MESS3 (0.091±0.009 mg/kg). Bench quality control material was measured at the start of each analytical run (set of 15 samples) for quality assurance and control. The measured values were, on average, within ±8% of the recommended values.

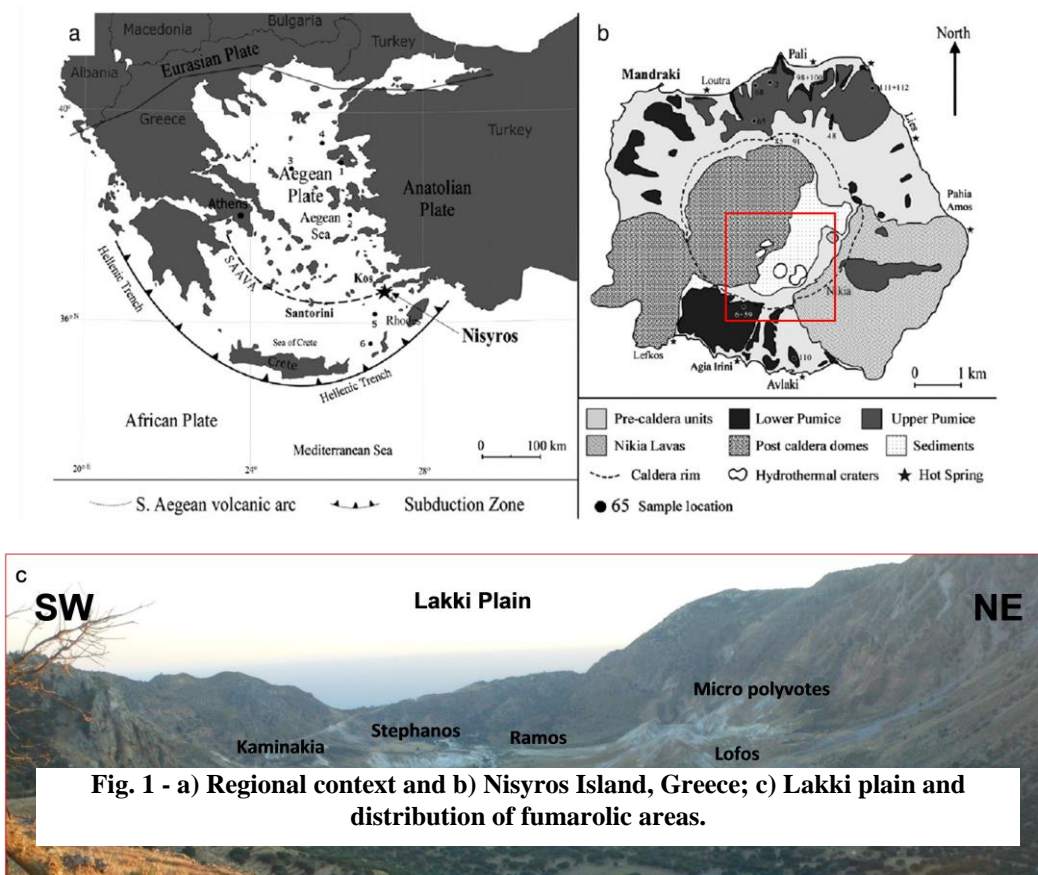


Figure 1 - a) Regional context and b) Nisyros Island, Greece; c) Lakki plain and distribution of fumarolic areas.

The simultaneous real-time measurements of Hg^0 , CO_2 , H_2S and meteorological parameters (air temperature, pressure and relative humidity) were carried out by coupling a portable Zeeman atomic absorption spectrometer with high frequency modulation of light polarization (Lumex RA-915M) and a Multi-GAS analyzer (manufactured by INGV-Palermo). The acquisition of the GPS signal at the same time allowed to obtain spatial coordinates for each concentration value. All instruments were synchronized and set to high-frequency acquisition (every two seconds). Measurements were carried out along three (Kaminakia, Stephanos and Lofos) transects-walk (about 15 km path, with a mean speed 1.5 km/h) across Lakki plain caldera.

All data were processed by GSA approach (Sinclair, 1974) and plotted by using GIS platform.

4. Results and Discussion

4.1. Soils

Hg data in soils, soil gases and real-time measures of Hg^0 , CO_2 and H_2S in the air were integrate to describe, as first step of a deeper study, the behavior of the hydrothermal gases once released and the Hg transportation processes through the soil and into the atmosphere.

Soil temperatures provided indication for the hydrothermal uprising gases, allowing to identify the anomalous areas. High temperatures were considered related to high fluxes of hydrothermal fluids and enhanced enrichment of the hydrothermal component in the soil gases. The temperature distribution map at 20 cm depth indicate temperature above 30°C at all the investigated sites, with the exception of some points along the western flank of Kaminakia crater. Higher temperature, in the range of 50 to 100°C were recorded at the southern part of Stefanos crater, at Phlegeton and Micro Polibotes (Fig. 2).

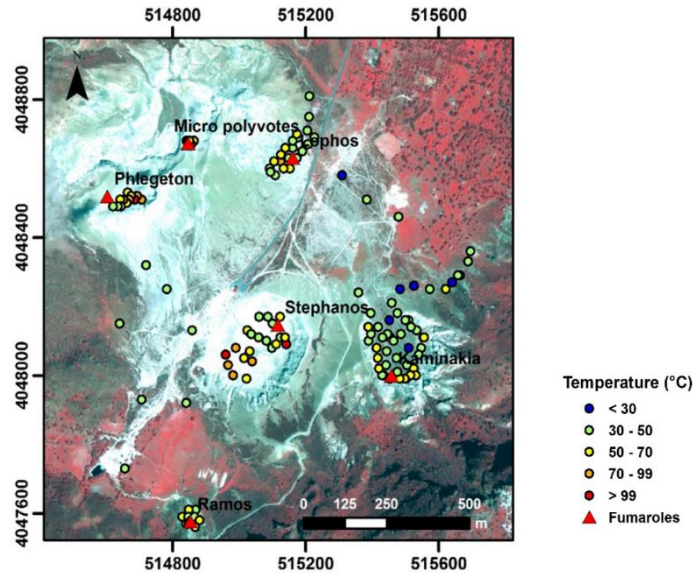


Figure 2 - Temperature distribution at Lakki Plain; temperature measurements were acquired at 20 cm depth.

The GSA approach (Sinclair, 1974) was applied on the CO₂ and H₂S dataset and the obtained probability plot allowed to estimate the source of the gas mixture. On the basis of CO₂ content, gases can be divided in three main families: background values (close to atmosphere), moderately high values (hydrothermal component and air mixing, CO₂ up to 47%) and very high values (hydrothermal component, CO₂ up to 75%) (Fig. 3). The H₂S probability plot shows the same three populations, the highest values being up to 18%.

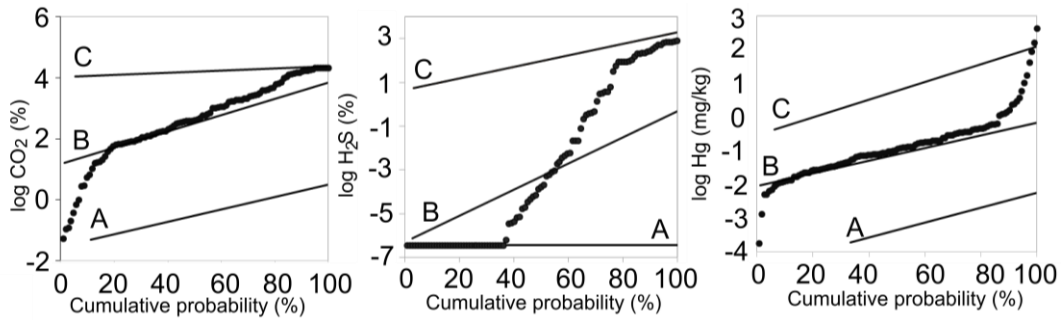


Figure 3 - Probability plots of CO₂ and H₂S in soil gases and total Hg in top soils.

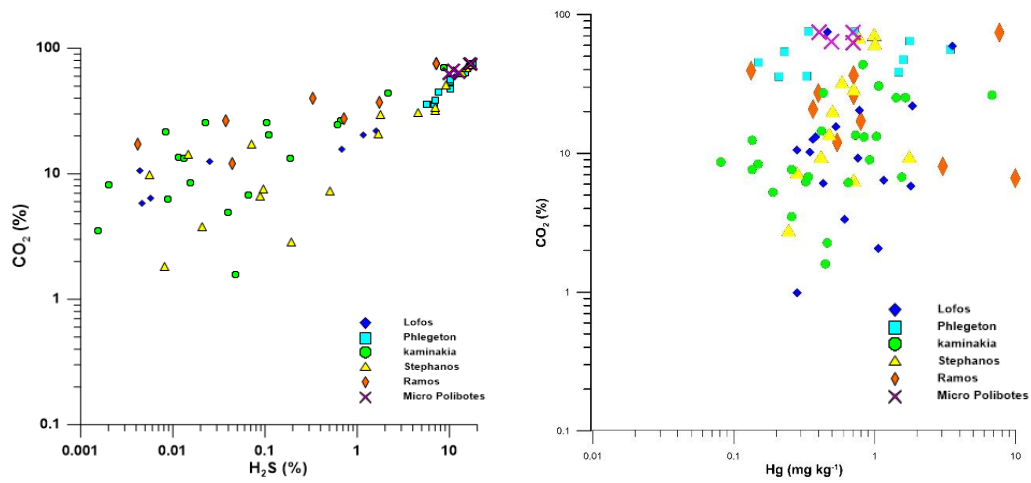


Figure 4 – CO₂-H₂S and CO₂-Hg binary plots.

The CO₂ and H₂S contents in the soil gases show a positive correlation, especially at high concentrations (Fig. 4). The general trend indicates that when CO₂ values are lower than 30%, H₂S content does not exceed 2% due to the influence of the diffusive flux. On the contrary, samples with CO₂ higher than 30%, show high H₂S concentrations, up to 18%, indicating that a convective regime and reducing condition dominate.

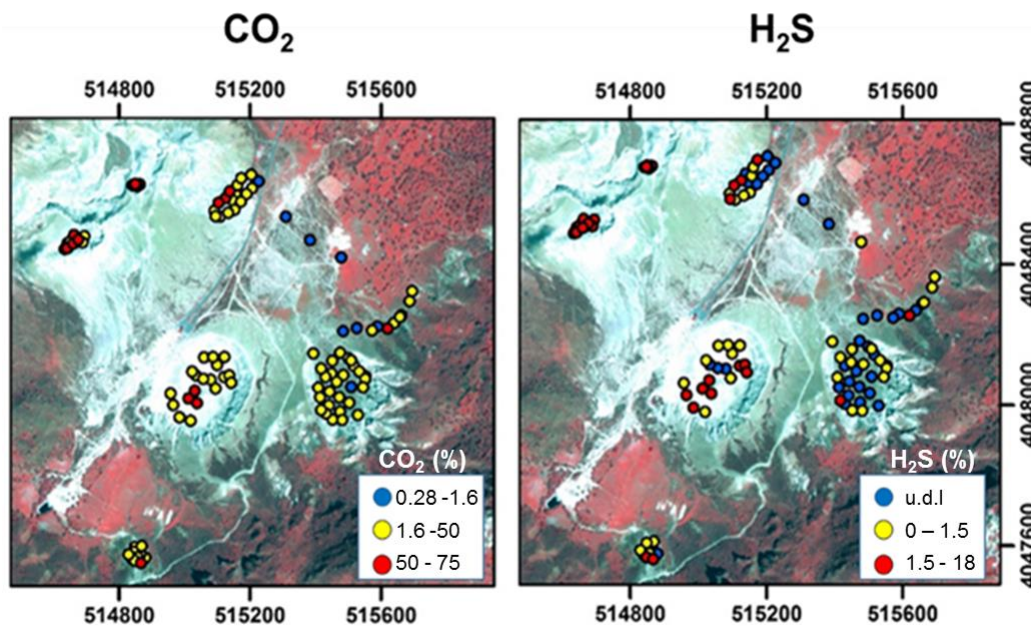


Figure 5 – CO₂ and H₂S distribution at the Lakki Plain in soil gases.

High concentrations of CO₂ and H₂S were measured at Phlegeton and Micro Polyvotés craters (Fig.5), with values close to the fumarolic compositions. Measurements at Lofos and Stefanos

craters showed variable concentrations of H₂S ranging from high concentrations, close to the relative fumarolic composition, down to concentrations below the detection limit.

The distribution of the temperatures and CO₂ and H₂S concentrations seems to be controlled by the fracturing pattern along the main NW- and NE-trending active fault systems, since the highest values were measured in correspondence of the main fumarolic manifestation, such as in the Stefanos, Micro Polyvotes and Phlegeton craters.

Soils were used to measure the total amount of Hg trapped in the soils; Hg value were plotted in a probability plot according to the GSA method and, as for CO₂ and H₂S, three population of data were detected. High Hg concentrations were also measured at the main fumarolic areas, without showing a clear correlation with CO₂ (Fig.4) and H₂S (not shown). It is worth noting that all samples have been taken at the same time and in the same place, but CO₂ and H₂S have been measured on the gas phase collected at 50 cm depth, while Hg has been measured on the solid phase at the soil surface. Nevertheless a better correlation was expected. The accumulation of Hg in the soil matrix does not depend solely on the amount of Hg carried by the upflowing hydrothermal gases but also on the capability of the soil to fix a part of it. Accumulation of Hg in soils depends on the amount of complexing phases within the soil. Mercury in soils shows generally a good correlation with soil organic matter (SOM) (Martin *et al.*, 2012 and references therein). The latter, which is the best Hg sink in the soil, was not determined in the soil samples of Nisyros but it is probably very scarce due to the absence of vegetation in the area. Sulphide, which could react with Hg, is also very scarce in the surface soil levels due to the oxidising environment (Daskalopoulou *et al.*, 2014). Soil temperatures are thought to play a role in Hg retention in soils. This parameter has probably a contrasting effect because higher soil temperatures indicate stronger hydrothermal gases that transport more Hg from depth, but at the same time higher soil temperatures presuppose also a faster remobilization of Hg from the soils because of its high volatility (Engle *et al.*, 2006).

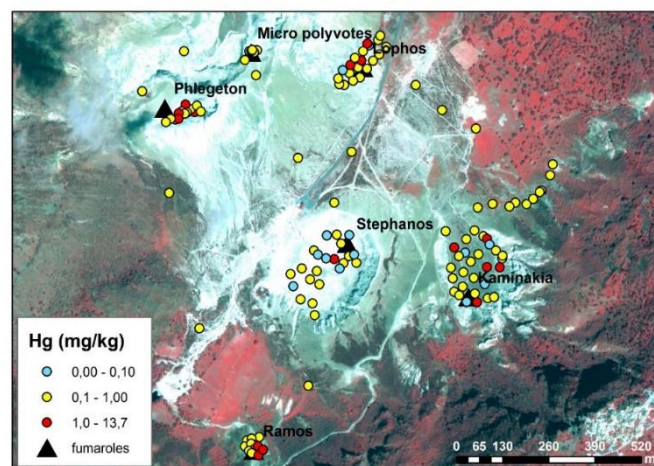


Figure 6 - Total Hg distribution in the top soils of Lakki Plain.

4.2. Atmosphere

The data acquired in the atmosphere were processed by using the GSA approach (Sinclair, 1974) and are showed in Figure 7. The CO₂ probability plot identifies three main populations (A, B and C). The A population groups value up to 440 ppm and refers to the background atmospheric CO₂. Population B (CO₂ up to 690 ppm) is the population with CO₂ level slightly higher than average atmospheric air, probably due to a weak degassing quickly diluted in the air. Population C includes the highest values (up to 4490 ppm) indicating a significant fumarolic contribution to the atmosphere.

Similarly to CO₂, H₂S probability plot suggests that the dataset can be divided in three populations; A includes very low H₂S concentrations, B values up to 30 ppm, indicating a significant H₂S emission into the atmosphere, and C population includes values reaching 63 ppm of H₂S in the air, suggesting the significant contribution of the hydrothermal fluids released from the subsurface. Also for Hg⁰ concentrations in the air, measured with the Lumex instrumentation, three populations were detected (A up to 16.5, B up to 40 and C up to 490 ng/m³).

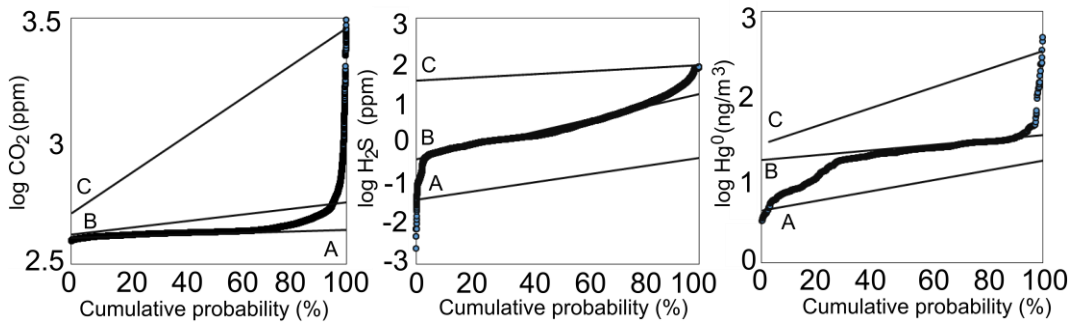


Figure 7 - Probability plots of CO₂, H₂S and Hg⁰ in the atmosphere.

In Fig. 8, atmospheric concentrations of H₂S, CO₂ and Hg⁰ against the number of measures over time, carried out through transect walk inside Stefanos crater, are shown. The main fumarolic emissions inside the crater were clearly highlighted by anomalously high Hg⁰ concentrations (up to ~500 ng/m³) with respect to the surrounding air masses (~30 ng/m³). Part of the released mercury is probably immediately retained within the soil, where it tends to form organo-metallic complexes (e.g. Landa, 1978). A good match between Hg⁰, H₂S and CO₂ concentration peaks was achieved, confirming the interdependence of these gaseous compounds and their common fumarolic origin. The variability in the continuous concentration signal probably depends on: i) different emission mechanisms among the gases, having a direct impact on their atmospheric dispersion (e.g. Witt et al., 2008); ii) the effect of wind direction and intensity; iii) the dilution of the fumarolic plumes; iv) the presence of multiple emission sources, which include both the fumaroles and the crater floor whose soil is characterized by a diffuse release of hydrothermal gases resulting also in the absence of vegetation.

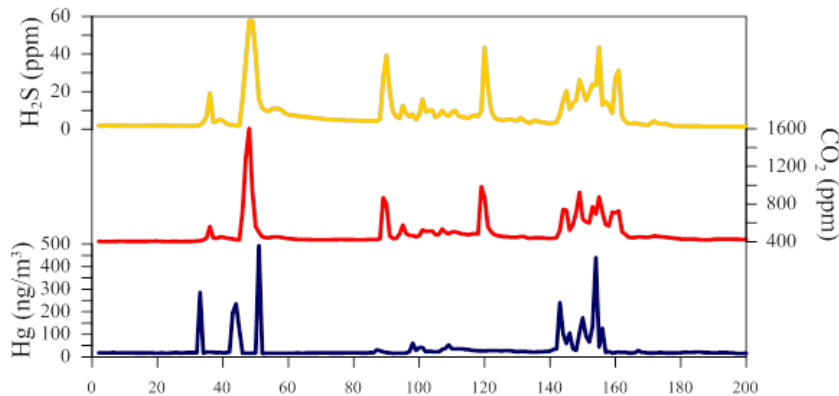


Figure 8 - CO₂, H₂S and Hg⁰ atmospheric concentrations against the number of measures over time within Stefanos crater.

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