

Elsevier Editorial System(tm) for Journal of Volcanology and Geothermal
Research

Manuscript Draft

Manuscript Number: VOLGEO2727R1

Title: Mercury concentration, speciation and budget in volcanic aquifers: Italy and Guadeloupe
(Lesser Antilles)

Article Type: Research Paper

Keywords: speciation, volcanic aquifers, total and dissolved mercury, mercury cycling, volatile
budget

Corresponding Author: Dr. emanuela bagnato,

Corresponding Author's Institution: University of palermo

First Author: Emanuela Bagnato, Dr

Order of Authors: Emanuela Bagnato, Dr; Alessandro Aiuppa, Prof; Francesco Parello, Prof; Walter
D'Alessandro, Dr; Patrick Allard, Prof; Sergio Calabrese, Dr

Abstract: Quantifying the contribution of volcanism to global mercury (Hg) emissions is important to understand the pathways and the mechanisms of Hg cycling through the Earth's geochemical reservoirs and to assess its environmental impacts. While previous studies have suggested that degassing volcanoes might contribute importantly to the atmospheric budget of mercury, little is known about the amount and behaviour of Hg in volcanic aquifers. Here we report on detailed investigations of both the content and the speciation of mercury in aquifers of active volcanoes in Italy and Guadeloupe Island (Lesser Antilles). In the studied groundwaters, total Hg (THg) concentrations range from 10 to 500 ng/l and are lower than the 1000 ng/l threshold value for human health protection fixed by the World Health Organization (WHO, 1993). Positive co-variations of (THg) with sulphate indicate that Hg-SO₄-rich acid groundwaters receive a direct input of magmatic/hydrothermal gases carrying mercury as Hg₀(gas). Increasing THg in a volcanic

aquifer could thus be a sensitive tracer of magmatic gas input prior to an eruption. Since the complex behaviour and toxicity of mercury in waters depend on its chemical speciation, we carefully determined the different aqueous forms of this element in our samples. We find that dissolved elemental $\text{Hg}^0(\text{aq})$ and particulate-bound Hg (HgP) widely prevail in volcanic aquifers, in proportions that highlight the efficiency of Hg adsorption onto colloidal particles. Moreover, we observe that dissolved $\text{Hg}^0(\text{aq})$ and $\text{Hg}(\text{II})$ forms coexist in comparable amount in most of the waters, in stark contrast to the results of thermodynamic equilibrium modelling. Therefore, chemical equilibrium between dissolved mercury species in volcanic waters is either prevented by natural kinetic effects or not preserved in collected waters due to sampling/storage artefacts. Finally, we provide a first quantitative comparison of the relative intensity of aqueous transport and atmospheric emissions of mercury at Mount Etna, a very active basaltic volcano.

Suggested Reviewers:



Università degli Studi di Palermo

DIPARTIMENTO DI CHIMICA E FISICA DELLA TERRA ED
APPLICAZIONI ALLE GEORISORSE E AI RISCHI NATURALI
(C.F.T.A.)

SEDE : Via Archirafi, 36 - 90123 Palermo
SEZIONE GEOFISICA : Via Archirafi 26 - 90123 Palermo

Journal of Volcanology and Geothermal Research
Editorial board

Dr. Emanuela Bagnato

e-mail : emanuelabagnato@virgilio.it
e. bagnato@unipa.it

Palermo, 06 October 2008

Dear Dr. Giovanni Chiodini,

I have pleasure in submitting the revised version of “Mercury concentration, speciation and budget in volcanic aquifers: Italy and Guadeloupe (Lesser Antilles)”, authors: E. Bagnato, A. Aiuppa, F. Parello, W. D’Alessandro, P. Allard and S. Calabrese, for consideration for publication in Journal of Volcanology and Geothermal Research.

Firstly we would like to thank the reviewers and the editor for the time that they took considering the manuscript. We have addressed the referees’ comments as detailed below (referee comments shown in italics). All the minor corrections have been accepted and the text has been modified (red text) according to the both reviewers’ suggestions.

#Reviewer 1:

1) Is anything known about, or you can say anything about, organic species of Hg in groundwater/hydrothermal fluids etc (e.g. monomethylmercury?). Would such Hg species be accounted for in the dissolved Hg budget, or not? And are they accounted for in the solution models of aqueous speciation?

1) Mercury methylation is the process that results in the conversion of inorganic Hg (especially Hg(II)) to methylmercury (CH_3Hg^+) by the action of anaerobic organisms (bacteria). The process can occur both in the water column and in the sediments and has been shown to be predominantly due to the sulphate reducing bacteria in freshwaters and estuaries. The biochemical pathways of methylation within hydrothermal features are poorly understood, and no much data are available in volcanic environments. However, preliminary research on the presence of methylmercury in geothermal springs (King et al., 2005) suggested that CH_3Hg^+ may account for less than 1% of the total Hg present in the groundwaters. The present manuscript is a first attempt to quantify Hg abundance in volcanic

aquifers and, in this case, we preferred not to investigate about methylated Hg species due to the complexity and the poor knowledge of Hg biogeochemistry and since sampling method and analysis are not still well defined. Obviously, methylation processes in the hydrothermal contexts are not to be excluded, but we think that the contribution of methylated Hg forms should not to account more in the dissolved Hg budget and the speciation models, but, anyway, it may results an important feature to investigate in the future works to better understand Hg cycle and distribution in volcanic environments.

2) *Fig 1c and Fig 6 to modify*

2) Left hand side of the fig 1c has been modified with “Sicily Channel”; and the name of the y axis of the fig 6a,b has been modified with moles/litre.

#Reviewer 2:

1) In various parts of the ms it is argued that Hg travels with the volcanic vapor phase and is absorbed into aquifers (I agree). The it is said that volcanic H₂S is also absorbed and later oxidized to SO₄. Why is SO₂ not mentioned as a potential S gas? S isotopes will show the precursor gas, which probably for many of these waters has been studied.

1) Groundwaters studied here are in most (all) cases representative of the shallowest parts of hydrothermal systems. Therefore, they are most-likely to dissolve/react with a low-T volcanic gas phase, which has previously been interacting (upon its ascent with deeper hydrothermal reservoir(s). In such circumstances, the low-T volcanic gas phase will have H₂S as its main S species (with SO₂ being scrubbed from and being converted to H₂S), even if the potential role of volcanic SO₂ is well documented. This concept has been mentioned in the revised ms (Line 398).

2) *What is endoreic?*

2) The reviewer is corrected here, the exact term is “endhoreic”, not endoreic, and it was used in the ms to indicate a closed basin that retains water and allows no outflow to other bodies of water such as rivers or oceans.

3) It is argued here that the main source for Hg in Etna waters is leaching from rocks. Later on, for Etna a comparison is made between vent Hg flux and aquifer Hg flux - if they have such a different origin, is this comparison valid? In the general correlation between SO₄ and Hg(tot), the Etna samples plot in the general array - why is Hg in Etna waters from rock leaching? If the CO₂ in groundwaters is ultimately derived from Etna volcanic gases, why is the Hg not from the gases but derived from the rocks?

3) We do not affirm that the source for Hg in Etna waters is rock leaching on the contrary we exclude that this source is significant. Maybe it was not correctly expressed in the ms so we changed the sentence of Line 277 from minor extraction to “negligible extraction”. The following referees considerations are therefore not relevant.

4) *Line 353- Waters may have carried more Hg than documented?*

4) We are sure enough that Hg has not been lost during our samplings and preservation of the samples, in particular for total and dissolved Hg data. Hence, the documented concentrations reported in the ms reflect those effectively found inside the investigated aquifers.

5) *Fig 4. log units (pH) versus linear units (Hg) - correlation diagram better in linear – linear*

5) We preferred to illustrate Fig.4 in the form log units (pH) versus log (Hg) for a better representation of the collected data which we'd have not obtained by a linear-linear correlation diagram.

Mercury concentration, speciation and budget in volcanic aquifers: Italy and Guadeloupe (Lesser Antilles)

E. Bagnato^{1,*}, A. Aiuppa^{1,2}, F. Parelo¹, W. D'Alessandro²,

5 P. Allard³, S. Calabrese¹

¹Dipartimento CFTA, Università di Palermo, Via Archirafi 36, 90123 Palermo, Italy

²INGV, Sezione di Palermo, Via La malfa 153, Palermo, Italy

³Laboratoire Pierre Sue, CNRS-CEA, CE-Saclay, 91191 Gif/Yvette, France

10

*Corresponding author. Tel.: +39091611574; fax: +390916168376

E-mail address: e.bagnato@unipa.it (E. Bagnato)

Abstract – Quantifying the contribution of volcanism to global mercury (Hg) emissions
15 is important to understand the pathways and the mechanisms of Hg cycling through the
Earth's geochemical reservoirs and to assess its environmental impacts. While previous
studies have suggested that degassing volcanoes might contribute importantly to the
atmospheric budget of mercury, little is known about the amount and behaviour of Hg
in volcanic aquifers. Here we report on detailed investigations of both the content and
20 the speciation of mercury in aquifers of active volcanoes in Italy and Guadeloupe Island
(Lesser Antilles). In the studied groundwaters, total Hg (THg) concentrations range
from 10 to 500 ng/l and are lower than the 1000 ng/l threshold value for human health
protection fixed by the World Health Organization (WHO, 1993). Positive co-variations
of (THg) with sulphate indicate that Hg-SO₄-rich acid groundwaters receive a direct
25 input of magmatic/hydrothermal gases carrying mercury as Hg⁰_(gas). Increasing THg in a
volcanic aquifer could thus be a sensitive tracer of magmatic gas input prior to an
eruption. Since the complex behaviour and toxicity of mercury in waters depend on its

chemical speciation, we carefully determined the different aqueous forms of this element in our samples. We find that dissolved elemental $\text{Hg}^0_{(\text{aq})}$ and particulate-bound Hg (Hg_p) widely prevail in volcanic aquifers, in proportions that highlight the efficiency of Hg adsorption onto colloidal particles. Moreover, we observe that dissolved Hg^0_{aq} and Hg(II) forms coexist in comparable amount in most of the waters, in stark **contrast** to the results of thermodynamic equilibrium modelling. Therefore, chemical equilibrium between dissolved mercury species in volcanic waters is either prevented by natural kinetic effects or **not preserved** in collected waters due to sampling/storage artefacts. Finally, we provide a first quantitative comparison of the relative intensity of aqueous transport and atmospheric emissions of mercury at Mount Etna, a very active basaltic volcano.

Keywords: *speciation, volcanic aquifers, total and dissolved mercury, mercury cycling, volatile budget*

40

1. Introduction

Volcanic degassing represents an important natural source of various toxic elements to the atmosphere and shallow aqueous systems (e.g. Pyle and Mather, 2003). Groundwaters circulating in active volcanic areas may contain appreciable amounts of trace metals as a result of their direct interaction with magma-derived fluids, the leaching of host volcanic rocks by gas-rich acid waters, or the leaching of ore deposits. The study of volcanic aquifers provides insights into the cycling of trace elements along various steps of the hydrological cycle, including the infiltration of meteoric waters into permeable volcanic layers, their interaction with rocks and uprising magmatic volatiles in a reducing and acid environment, and the final discharge to the surface. Furthermore, the determination of potentially harmful elements in volcanic aquifers is crucial because these often constitute an important water resource for **local communities**.

55 Mercury is one of these harmful elements. It is a highly volatile and toxic trace metal
that is released into the hydrosphere, atmosphere and biosphere through both
anthropogenic and natural processes, the latter including degassing from active
volcanoes (Siegel and Siegel, 1984; Fitzgerald, 1986; Mason *et al.*, 1994; Pyle and
Mather, 2003). In the atmosphere, mercury is transported in its volatile (elemental
60 gaseous mercury Hg^0), reactive (Hg(II)) and particulate-bound (Hg_p) forms (Lin and
Pehkonen, 1999a,b; Lindqvist and Rodhe, 1985). In the marine and terrestrial
environments, inorganic Hg is often methylated to methylmercury species which readily
accumulate in marine organisms (Slemr *et al.*, 1985; Fitzgerald *et al.*, 1986, 2003; Lee
and Iverfeldt, 1991). In groundwater environments, mercury is known to bio-
65 accumulate and to become very dangerous to human health when exceeding threshold
concentrations in **drinking water** (Nriagu and Becker, 2003; Ikingura and Akagi, 1999).
The toxicity of this element strongly depends on its chemical form and, owing to its
complex geochemical behaviour, determining its speciation in groundwaters requires
appropriate techniques for sampling and preservation of aqueous samples (Parker and
70 Bloom, 2005). Analysis of Hg species in water can be made by studying the mercury
distribution between total, dissolved and particulate-bound forms within an aquifer
system. Since mercury often occurs at very low concentrations in natural waters, serious
problems can often arise from sampling and post-sampling procedures, due to possible
losses or contamination during storage.

75 The mercury speciation in volcanic groundwaters is still poorly characterised, and
very few data exist for the mercury content in hydrothermal systems (Varekamp and
Buseck, 1986; Christenson and Mroczek; 2003). Therefore, our objective in this study
has been to determine both the concentration and the speciation of mercury contained in
selected volcanic aquifers, in order to improve our current understanding of Hg hydro-
80 cycling in volcanic environments. Using the analytical procedures established by Parker

and Bloom (2005), we measured the concentrations of total (THg), dissolved (HgD) and particulate (Hg_p) mercury in water samples from volcanic aquifers located in Southern Italy (Mt. Etna, Sicily, and Vulcano, Stromboli, Ischia and Pantelleria volcanic islands) and the Lesser Antilles (Soufriere volcano, Guadeloupe island). We also provide a new
85 estimate of the proportions of [Hg(II)] and Hg⁰_{aq} species among the dissolved forms of mercury in volcanic aquifers. Finally, we quantitatively assess the mass budget of aqueous transport of mercury at Mount Etna and its contribution to the bulk Hg budget of that very active basaltic volcano.

90 2. Studied sites and methods

2.1 Studied sites

The volcanoes of Southern Italy and Guadeloupe whose **aquifers we studied are all** actively degassing. They are representative of different volcanic activity level, ranging
95 from open conduit degassing with frequent eruptions at Etna and Stromboli to quiescent hydrothermal manifestations at Vulcano, Pantelleria, Ischia and La Soufrière. These volcanoes are fed by different magma types (from basalt to andesite) and are located in distinct geodynamic contexts (tensional fracturing or rifting for Etna and Pantelleria, subduction zones for all other ones). Below we summarize the main features of these
100 different volcanic sites:

(a) Mt. Etna is a very active and large (40 km wide, 3.3 km high) alkali basaltic strato-volcano, that has built since 0.6 Ma on tensional tectonic faults on the Eastern coast of Sicily (Fig. 1). It produces frequent summit and flank eruptions (e.g. Allard *et al.*, 2006) and continuously releases huge amounts of magmatic volatiles from its summit craters,
105 which makes it one of the strongest volcanic emitters of many volatile species with potential environmental impact (Allard *et al.*, 1991; Gauthier and Le Cloarec 1998;

Caltabiano *et al.*, 2004). Its groundwater system is extensive and **has been the subject of several** chemical and isotopic studies (see Aiuppa *et al.*, 2004, and references therein).

(b) Stromboli is the most active volcano of the Quaternary Aeolian island arc, north of Sicily (Fig. 1), beneath which the Ionian oceanic plate is still subducting. It is a 3 km high, prevalently submarine basaltic strato-volcano **whose upper part**, Stromboli island (3-4 km in diameter, 924 m high), emerges from the Tyrrhenian sea. Its feeding magmas have a calc-alkaline to shoshonitic affinity and range in age from approximately 0.2 Ma to present (Hornig-Kjarsgaard *et al.* 1993). Quiescent and explosive gas emissions from Stromboli craters are approximately one order of magnitude lower than those from Mt. Etna, but are representative **of** erupting arc volcanoes (Allard *et al.*, 1994, 2000). Thermal waters (~40°C) diluted by sea water occur along its southeastern coast.

(c) Vulcano island is located in the southern-central part of the Aeolian Arc (Fig. 1). Since its last explosive (vulcanian) eruption, in 1888–1890, its active cone (La Fossa) has continued to be the site of intense fumarolic activity. Intermittent periods of increasing fumarole temperatures (up to 700°C) and spatial extension, connected with seismic activity, occurred in the 1920s then between 1978 to the present day (Barberi *et al.* 1991; Paonita *et al.* 2002). The composition of the fumarolic gases results from the mixing of magmatic gas with hydrothermal and seawater-derived fluids (Paonita *et al.* 2002; Chiodini *et al.*, 2000). A very active hydrothermal system, tapped by wells or manifested by thermal springs, surrounds the active volcanic cone.

(d) Pantelleria volcanic island (83 km², 836 m a.s.l.) is located 100 km SW of Sicily and 70 km off the Tunisian coast (Fig.1), on the axis of the Sicily Channel tensional rift zone. This large strato-volcano, topped with a caldera, is quiescent at present but six eruptive cycles have been recognized in the last 50 ka at Pantelleria (Civetta *et al.*, 1984). Its most recent eruption was submarine and happened 3 km NW of the island in October-December 1891 (Washington, 1909). Widespread thermal manifestations on

Pantelleria attest to a sustained heat flow and have been the subject of a few previous studies (Parello *et al.*, 2000). Many hot springs and thermal wells (30-81°C) are distributed in the NE and SW sectors of the island, most of which lie along the coastline.

(e) Ischia is the westernmost active volcanic complex of the Campania area and belongs to the **Phlegrean** volcanic district, which also includes Campi Flegrei and Procida (Fig.1). Many thermal manifestations and **modest** seismic activity characterize the current activity of the island (Caliro *et al.*, 1999). Thermal waters, submarine and subaerial fumaroles are well known since Roman times and still constitute an important touristic and economic resource for the island.

(f) Finally, Guadeloupe island, located on the eastern margin of the Caribbean plate (Bouysse, 1988) (Fig.1), belongs to the intra-oceanic Lesser Antilles volcanic arc..Its currently active volcano, La Soufrière, **is** an andesitic complex with lava domes and cones. Since its last magmatic eruption in 1530 (Komorowski *et al.*, 2001), La Soufrière volcano has maintained a very intense hydrothermal activity punctuated by a series of violent phreatic eruptions (Boudon *et al.*, 1989; Komorowsky *et al.*, 2001). At present, strong fumarolic degassing, generating plume emissions (Bernard *et al.*, 2006), occur from the summit of the lava dome and numerous thermal springs are distributed within 0.5-5 km distance around the lava dome. Historical observations showed that the nature, distribution, and intensity of these geothermal manifestations have fluctuated considerably over time and He-carbon isotopic measurements demonstrate a magmatic origin of the gases (Allard, 1983; Allard *et al.*, 2000).

155

2.2. Sampling and analytical methods

Twenty-two water samples were collected at Mt Etna (springs, wells and drainage galleries), 9 samples on Vulcano (wells), 27 thermal waters on Ischia (wells and

springs), two (thermal water wells) on Stromboli, 10 samples on Pantelleria (wells and
160 springs) and 9 thermal springs around Soufriere volcano in Guadeloupe.

In order to avoid **mercury contamination**, waters were collected and stored in
completely **fully filled** glass bottles with Teflon-lined caps that were pre-cleaned in
laboratory by soaking them with a 10% HNO₃ solution for about 48 hours, then rinsed
several times with Hg-free MilliQ water and dried in a class 100 fume hood (Bloom *et*
165 *al.*, 1988). One bottle blank was always analyzed for each batch in order to check the
cleaning procedure. During sample collection, bottles were rinsed three times in the
field with sampling water before being filled.

General water quality parameters (pH, Eh, T, Electric Conductivity) were measured
in the field with portable instruments. Major element analysis (Na, K, Mg, Ca, Cl, NO₃
170 and SO₄) was made at INGV-Pa by Ionic Chromatography while total Alkalinity was
determined by titration with HCl 0.1M. The chemical composition of the investigated
volcanic groundwaters is reported in Table 1.

Total mercury analysis was made on unfiltered water, while samples for the
determination of dissolved Hg were filtered through 0,20 µm filters. Both were acidified
175 with 0,4% (v/v) ultra-pure HCl and stored **refrigerated in the dark**. Total and dissolved
mercury were analysed at C.F.T.A. Dept. in Palermo using BrCl oxidation, SnCl₂
reduction, dual amalgamation, and cold vapour atomic fluorescence spectrometry
(CVAFS), according to the U.S.EPA Method 1631 (Bloom *et al.*, 1988). A Tekran 2600
analyzer **with** gold quartz-sand traps was used for pre-concentrating mercury. Our
180 detection limit (MDL) is 0.5 ng l⁻¹ and the analytical reproducibility is ±10%.

Divalent ionic mercury [Hg(II)], was determined by analyzing fresh, un-acidified and
un-oxidized water samples that were reduced with SnCl₂ by means of the same
apparatus (Parker and Bloom, 2005). The Hg analyzer was calibrated using a five-point
calibration curve, and inorganic Hg standards were prepared by direct dilution of NIST-

185 certified 10,000-ppm aqueous Hg standard solution. Particulate mercury content in
waters (Hg_p) was estimated as the difference between the measured total and dissolved
mercury concentrations, according to EPA 1631 method procedure. The results are
given in Table 1.

190 **3. Results**

3.1 Groundwaters chemistry

On Mt. Etna, water samples were collected at different elevations and distributed
over an area of about 1200 km². The sampled waters are characterised by low
195 temperatures (mean about 16°C) and pH values ranging from 6.07 to 7.56. Previous
isotopic studies (Allard *et al.*, 1997; D'Alessandro *et al.*, 2004) have demonstrated the
meteoric origin of Etnean groundwaters. The chemical composition of Mt. Etna
groundwaters is strongly controlled by the dissolution of magma-derived CO₂ in the
aquifer, which in turn promotes intense acid leaching of the host basaltic rocks. This
200 process, which takes place in a cold environment, is responsible for the typical
bicarbonate-alkaline to alkaline-earth chemical composition of groundwaters in the
volcano's aquifers (Fig. 2a,b). The amount of metals that are released into the
groundwaters depends on the intensity of the water-rock interaction processes inside the
aquifer (Aiuppa *et al.*, 2000).

205 The two thermal waters sampled on Stromboli Island (Fulco and Zurro wells) have
temperatures of 42° and 36°C and pHs of 6.36 and 7.00, respectively. Both samples
have a Na-Cl composition (Fig. 2a,b) and are interpreted as mixtures of bicarbonate-rich
meteoric water and seawater (TDS between 17,500 and 18,800 mg/l) (Carapezza and
Federico, 1999). Their high HCO₃ content (between 253 and 652 mg/l) reflects the input

210 of magmatic-derived CO₂, as evidenced by the isotopic ratios of dissolved CO₂ and He (Inguaggiato *et al.*, 2004).

The sampled groundwaters on Vulcano Island have temperatures ranging from 22° to 61°C and pH values between 6.36 and 7.8. They display a wide compositional range, from sulphate-chloride-alkaline to sulphate-chloride-earth-alkaline waters (Fig. 2a,b).
215 The origin of their high contents in either Cl or SO₄ remains a matter of debate (Bolognesi and D'Amore, 1993; Capasso *et al.* 2001): NaCl groundwaters (Castello, EAS) are attributed to either sea-water intrusion in the Vulcano Porto area (Fig. 2a,b) or the ascent of NaCl hydrothermal brines (Bolognesi and D'Amore, 1993). Sulphate-rich groundwaters are instead interpreted as being meteoric waters steam-heated by H₂S-rich
220 hydrothermal fluids, boiled off from the reservoirs at depth (Aiuppa *et al.* 2000; Capasso *et al.* 2001).

The chemistry of Pantelleria's thermal waters is mainly dominated by a mixing process between meteoric water and seawater-dominated thermal waters, a process that gives rise to chloride-alkaline compositions (Fig. 2a,b). The thermal waters were shown
225 to derive from a large hydrothermal system reaching about 250°C at 1.5-2 km depth (D'Alessandro *et al.*, 1994; Fulignati *et al.*, 1997). The collected water samples represent partially-equilibrated fluids (Giggenbach, 1988), with Na-K equilibrium temperatures of 180 to 200 °C. Highly concentrated NaHCO₃-rich solutions with high pH (8.44-9.25) occur in Specchio di Venere Lake, an endoreic basin.

230 Thermal waters from Ischia island have contrasting compositions, from bicarbonate-rich (HCO₃ from 171 to 2110 mg/l) to chloride-rich (Cl from 91 to 19000 mg/l) (Fig. 2a,b). The bicarbonate waters are representative of local meteoric groundwaters variably heated by interaction with CO₂-rich vapours of deep origin. These waters exhibit temperatures from 28 to 67 °C, TDS from 1270 to 4420 mg/l, and pCO₂ values from 2.3
235 to 6.3 atm. Chloride-rich groundwaters are characterized by temperatures of 26 to 91

°C, have high TDS (max value 38200 mg/l) and Na as the main cation. These fluids represent mixtures of meteoric water and sea water that are variably heated and chemically modified at depth within the hydrothermal system (Aiuppa *et al.*, 2006).

At La Soufrière volcano, the distribution of thermal springs around the summit lava dome is controlled by the topography of the basement and the occurrence of argillitic hydrothermal alteration zones. The collected waters are characterized by temperatures from 21° to 58°C and pH values between 4.93 and 6.43. Our and previous data indicate that Ca-SO₄ waters (Fig. 2a-b) prevail close to the lava dome (Bain Jaunes, Carbet l'Echelle, Galion and Matouba). These steam-heated waters result from the interactions of meteoric groundwater with CO₂-H₂S-rich vapour of magmatic origin, whose condensation gives rise to highest HCO₃⁻ and SO₄²⁻ contents in the most proximal spring of Carbet l'Echelle. Instead, Ca-Na-HCO₃ waters (Habitation Revel) correspond to shallow groundwaters that interact with a cold CO₂-rich magmatic gas phase. Finally, Ca-Na-Cl waters (Chutes du Carbet) are interpreted as a mixture between Ca-SO₄ waters and Na-Cl waters (Villemant *et al.*, 2005). The lack of systematic correlations between halogens (Cl, Br, and F) and cation contents indicate that seawater contribution can be ruled out. Previous studies ascribed the excess of halogens to a mixing process between meteoric water and a true magmatic component that transports Cl⁻ and Br⁻ ions from a deep gas source to the shallow aquifers (Boichu *et al.*, 2008; Villemant *et al.*, 1999).

3.2. Mercury content in groundwaters

The total Hg content of all analysed groundwaters cover a wide range from about 10 to 500 ng/l (Table1). Such concentrations are below the threshold value of 1000 ng/l that was set by the World Health Organization (WHO) for human health protection. The abundances of mercury in natural waters depend on many factors such as temperature,

pH, the highly volatile nature of the element, and its tendency to be adsorbed onto clays, iron and manganese hydroxides and organic matter (Jenne, 1970). The simultaneous action of these factors, combined with the low abundance of mercury in crustal rocks (10⁻⁶-10⁻⁴ wt%; Fleisher, 1970), account for the very low and variable mercury concentrations often exhibited by natural waters. We explore thereafter the influence of these factors on the mercury content and speciation in our volcanic water samples.

3.2.1. Mt. Etna

Etna's groundwaters have a variable but generally low mercury content (Table 1), with THg values ranging from 4 to 34 ng/l and averaging ~14 ng/l. HgD content averages 8 ng/l (range 1.5-25) and particulate mercury (Hg_p) 7 ng/l (range 2.5-28). The latter accounts for about 50% of THg, while Hg⁰_{aq} represents the main aqueous species (60 to 100% of HgD). These relatively high proportions of Hg⁰_{aq} probably reflect the reduced conditions (low pO₂) of the waters (Varekamp and Buseck, 1984). The overall low mercury content of Etnean groundwaters is consistent with their low temperatures (10-20°C) and negligible extraction of Hg from the aquifer rocks during low-temperature underground water-rock interactions. In contrast, the hypothermal brines discharged at "Salinelle" display higher mercury contents, with THg and HgD concentrations of 112 ng/l and 74 ng/l, respectively. Particulate Hg content was evaluated as about 38 ng/l, while Hg⁰_{aq} content is 53 ng/l. The higher concentrations of mercury in these brines can be related to both their reduced conditions (Eh = -17 mV), high chloride content (Cl = 41200 mg/l), and the higher equilibrium temperature (T~140°C) estimated for their feeding hydrothermal reservoir. In fact, the formation of Hg-Cl complexes in saline waters (Khodakovskii *et al.*, 1981) enhances Hg aqueous transport.

3.2.2. *Stromboli*

The two thermal water wells, Zurro (35°C) and Fulco (41°C), we sampled on
290 Stromboli island have slightly-acidic pH, reducing redox potentials and high SO₄
contents (1200 and 1400 mg/l, respectively). Their concentrations in mercury are much
higher than those generally found in Etna groundwaters (Table 1), with mean THg and
HgD values reaching 195 and 33 ng/l, respectively. Hg(II) species amount to 3.8 and
18.4 ng/l and particulate Hg_p (182 and 141 ng/l) prevails over the dissolved Hg forms,
295 which points to a prevalent transport of mercury in the suspended colloidal phase in
these thermal waters.

3.2.3. *Vulcano*

Vulcano groundwaters display average THg and HgD concentrations of 45 ng/l
300 (range 11-139) and 6.6 ng/l (range 2.7-18.4), that are intermediate between those for
Etna and Stromboli (Table 1). THg correlates positively with SO₄ (Fig. 3) and
negatively with the water redox potential; the highest THg content (139 ng/l) is detected
in Castello sample that is also among the richest in SO₄ (1680 mg/l) and the more
reducing ones (Eh = - 250 mV). Quite high THg are also found in Discarica (77 ng/l)
305 and Bartolo (65 ng/l) SO₄-rich waters, which are also characterised by reducing and
acidic conditions. Most of the mercury present in Vulcano groundwaters occurs as
Hg(P): this latter averages about 38 ng/l (range 3.4-133) and is the most concentrated in
Castello (133 ng/l), Discarica (75 ng/l) and Bartolo (54 ng/l) waters. Particulate mercury
(Hg_p) contributes the complement to the highest measured total Hg contents. In most
310 waters Hg(II) is the main dissolved species, accounting for 40 to 100% of HgD and
averaging 5.6 ng/l (range 3-10). Again, **the larger proportion of the** Castello sample
stands out for its much larger proportion of Hg⁰_{aq} (about 60% of HgD), in agreement
with its more reducing conditions (Table 1).

315 3.2.4. *Pantelleria*

On Pantelleria island thermal waters have modest THg concentrations (average: 22 ng/l, range from 12 to 47 ng/l), and a mean dissolved mercury (HgD) content of about 10 ng/l (range 2-15) (Table 1). The highest THg values are found at Buvira Rizzo (47 ng/l) and in the Specchio di Venere lake (41 ng/l) within and around which intense gas
320 manifestations do exist. Particulate mercury Hg_p contributes quite variable proportions of THg (range: 0.5 to 45 ng/l, and mean: 12 ng/l; Table 1). Hg(II) varies from 2 to 9 ng/l (mean: 5), while Hg^0_{aq} ranges from 0.16 to 10 ng/l (mean: 4).

3.2.5. *Ischia*

325 Ischia thermal waters exhibit a great variability in Hg content, in agreement with the wide temperature and compositional range of the waters constituting the aquifer (Table 1 and Fig. 2a,b). THg vary from 1.1 to 205 ng/l (mean: 45 ng/l) and HgD from 0.9 to 169 ng/l (mean: 22 ng/l). Particulate mercury represents a minor proportion of THg (mean: 21 ng/l, range: 0.5-113 ng/l) when comparing to other volcanic aquifers. Among
330 the dissolved species, Hg^0_{aq} (range 1.8 - 39 ng/l, mean 14 ng/l) is the most abundant one. Hg(II) contents vary from 1.6 to 153 ng/l (mean: 12.5 ng/l).

3.2.6. *La Soufriere volcano (Guadeloupe)*

Thermal springs surrounding La Soufrière lava dome are the richest in mercury
335 among all the waters analysed in this study (Table 1). Their THg and HgD contents respectively average 230 ng/l (range: 10 to 494) and 133 ng/l (range: 9 to 247). Hg_p varies from 1 to 358 ng/l (mean: 137 ng/l) and accounts for 10 to 90% of total mercury. Hg^0_{aq} (4.2 to 296 ng/l, mean: 125 ng/l) is generally the main aqueous Hg species, Hg(II) contents averaging only 8 ng/l. At La Soufrière there is a clear negative dependency of

340 THg on pH (Fig. 4). The most acidic (pH <6) groundwaters, issuing at the base of the
lava dome (Carbet l'Echelle, Ravine Marchand, Pas du Roy, Bains jaunes and Galion),
are typically the most enriched in mercury (Table 1). These waters are also the richest in
sulfate and display low redox conditions (Eh between -100 and 100 mV) and low TDS
content (366 to 2683 mg/l). Therefore, as already suggested for Vulcano waters, the
345 positive correlation between THg and SO₄ (Fig. 3) in La Soufriere thermal waters
supports the idea of that most of the mercury is directly supplied as Hg⁰ by CO₂-H₂S-
rich vapours of magmatic origin that condense in the aquifers while reacting with
groundwater.

350 4. Discussion

4.1 Factors and processes controlling the abundance of Hg in volcanic aquifers

Mercury can be supplied to volcanic groundwaters by several processes, such as
direct input of Hg-bearing fluids of magmatic origin, the raise of Hg-rich hydrothermal
355 steam boiled-off by hydrothermal brines at depth, and water-rock interactions in hot and
acid hydrothermal aquifers. At the surface and in groundwaters, Hg availability is a
complex function of many factors: total concentration and “speciation” of the metal
itself, mineralogy of the host rocks, pH, redox potential, temperature, total organic
content, suspended particulate abundance and aquifer discharge rate (Watras *et al.*,
360 1994; Sarkar *et al.*, 2000). Such a complex behaviour of mercury in hydrothermal-
volcanic environments is clearly reflected in its wide concentration variations in thermal
waters analysed in this study (Tab. 1) and previously (Varekamp and Buseck, 1984;
Christenson *et al.*, 2003; Herdianita and Priadi, 2008).

No first order cause-effect relationship can explain the extreme variability, by several
365 orders of magnitude, of mercury concentrations in the studied volcanic aquifers. First,

the measured total (THg) and dissolved (HgD) mercury concentrations are independent on the groundwater discharge temperature. Since solubilities of Hg-S minerals and Hg_(l) are positively correlated with temperature (Varekamp and Buseck, 1984), the lack of systematic Hg-temperature correlation argues against a control of Hg aqueous contents

370 by any mineral-solution equilibrium process in the studied aquifers. On the other hand, a peculiar dependency of THg on groundwater pH is observed (Fig. 4): groundwaters with THg > 100 ng/l are systematically characterised by acid to neutral pH values (from 4.9 to 7), while THg concentrations in neutral to basic environments (pH from 7 to 9.11) are typically < 65 ng/l. Two main factors may account for this observation:

375 (i) Groundwater pH is the main factor controlling Hg adsorption onto mineral surfaces. It has been demonstrated (Anderson, 1979) that surface adsorption of mercury is minor at low pH values, but favoured in alkaline oxidised environments. Owing to the very high affinity of mercury for adsorption onto clay minerals and iron oxy-hydroxides, which are among the main secondary phases formed by low-temperature weathering of

380 volcanic rocks (Aiuppa *et al.*, 2000), heterogeneous surface reactions could be a determining factor in controlling Hg hydrocycling in volcanic aquifers.

(ii) In a volcanic aquifer, groundwater pH is determined by the amount and rate of dissolution of reactive and acidic gases, such as CO₂, SO₂, H₂S and HCl, and by the extent of water-rock interaction. In general, low pH and p_e values are typical of the

385 initial stages of gas-water-rock interaction, during which the dissolution of acid magmatic/hydrothermal gases in groundwater promotes intense and isochemical leaching of the host-rocks (Giggenbach, 1988). With increasing extent of gas-water-rock interaction, pH and p_e values tend to increase due to their buffering by rock dissolution and interaction with atmospheric gases. Accordingly, it can be argued that

390 high Hg contents in volcanic waters may date to the pristine stages of gas-water-rock interaction, during which mercury originally transported as volatile Hg⁰_{gas} (Varekamp

and Buseck, 1984) is primarily provided by condensation of magmatic/ hydrothermal vapours. This process can prevail as long as the input of deep fluids is maintained and fresh (un-altered) volcanic rocks remain available. Along with more extensive
395 interaction with the host rocks (e.g., when groundwater residence time in the aquifer is long enough or when reactive gases become less abundant), oxidizing and basic environments are gradually formed, promoting Hg^0 oxidation to Hg(II) and thus the scavenging of Hg adsorbed onto mineral surfaces. Groundwaters studied here are in most (all) cases representative of the shallowest parts of hydrothermal systems.
400 Therefore, they are most-likely to dissolve/react with a low-T volcanic gas phase, which has previously been interacting (upon its ascent with deeper hydrothermal reservoir(s)) In such circumstances, the low-T volcanic gas phase will have H_2S as its main S species (with SO_2 being scrubbed from and being converted to H_2S).

The positive correlation between THg and SO_4 depicted in Figure 3 provides strong
405 evidence that aqueous Hg is generally contributed from a Hg-rich gas precursor. In fact, this correlation is especially clear at volcanic sites such as Vulcano, Stromboli and La Soufriere, where continuous supply of magmatic heat and magma-derived volatiles directly sustains intense fumarolic discharge and hydrothermal circulation. At these volcanoes, high sulphate contents in thermal waters are systematically associated with
410 low pH and Eh, and therefore are consistent with groundwater heating by condensation of H_2S -bearing hydrothermal steam, followed by H_2S oxidation by atmospheric gases (Giggenbach, 1988). Hence, the co-variation of THg and sulphate in these “steam-heated groundwaters” strengthens our conclusion that Hg-rich volcanic waters result from a direct feeding by magmatic/hydrothermal vapours. We suggest that Hg is mainly
415 contributed to the aquifer as Hg^0_{vap} , transported by the uprising CO_2 and H_2S -rich geothermal/magmatic steam. Upon interaction with the aquifer, Hg^0_{vap} is dissolved as Hg^0 , and partially oxidised to Hg(II) aqueous forms due to the oxidizing conditions of

shallow groundwaters. A non-negligible part of the oxidized Hg forms can eventually be adsorbed onto the particulate (colloidal) phase.

420

4.2 Mercury speciation in volcanic waters: experimental and model evidences

The measured speciations of mercury in our water sample set provide important constraints on the partitioning of this element between its various ionic and particulate forms. The results of analytically-determined Hg speciation are summarised in Figure 5a-c. Figure 5a demonstrates a positive correlation between THg and HgD concentrations, the former prevailing over the latter, which validates the reliability of our analytical procedures. This correlation also implies that particulate-bound mercury (Hg_p), calculated as the difference between THg and HgD, constitutes an important fraction of THg, averaging about 50% (Fig. 5b). The HgD/Hg_p ratio however displays a great variability from 0.05 to 56 (Fig. 5b). Samples from Vulcano are systematically enriched in Hg_p, whereas the opposite is observed on Pantelleria and Ischia: there, HgD generally exceeds Hg_p, likely because the high TDS and Cl contents of these groundwaters (Table 1) enlarge the stability field of dissolved forms such as HgCl₂.

Our results also provide new insight into the relative abundances of the dissolved forms (Hg⁰_{aq} and Hg(II)) of mercury. Figure 5c demonstrates a great variability in the proportions of these two dissolved forms, even though they occur in nearly equal amount on average. To summarise, the following conclusions can be derived from our experimental determinations of Hg speciation:

- (i) Dissolved and particulate forms are typically present in equal amounts in the studied groundwaters, highlighting the important role played by adsorption processes on colloidal particle surfaces;
- (ii) Dissolved Hg⁰_{aq} and Hg(II) forms also occur in comparable amounts in most of the investigated groundwaters, but display large variations in some other waters.

The experimentally-determined Hg speciations discussed above can be compared
445 with theoretical equilibrium activities of dissolved Hg in groundwaters under the
measured T, pH, and $p\epsilon$ conditions, computed by using the PHREEQC speciation
software (Parkhurst, 1995). Such a comparison allows us to check whether Hg species
either reach or not thermodynamic equilibrium in the aqueous phase. For these
computations, we used a modified version of the WATEQP thermochemical database
450 (Appelo, 1988), implemented with thermochemical data from the HSC database (HSC,
1999) for the most relevant aqueous and condensed Hg species. Figure 6a shows the
computed equilibrium molar concentrations of Hg_{aq}^0 and Hg(II) for the investigated
groundwaters, as calculated with PHREEQC, versus the corresponding redox potential
(given by groundwater $p\epsilon$). The diagram indicates that Hg_{aq}^0 should be the main
455 equilibrium Hg aqueous form in all studied waters (molar abundance $\sim 10^{-10}$), as also
inferred for some thermal waters in New Zealand (Christenson et al., 2003). Hg(II)
increases with increasing $p\epsilon$ values, but remain several orders of magnitude lower than
 Hg_{aq}^0 at equilibrium, even in oxidizing conditions (range: 10^{-34} to 10^{-14} M). HgCl_2
prevails among the Hg(II) species, depending on the water Cl content (Fig. 6b).

460 Comparison between Figures 5c and 6a clearly demonstrates that our analytical
results are in stark contrast with the computed equilibrium speciations: the relative
proportions of measured Hg(II) are far larger than those expected at equilibrium in the
T, pH, $p\epsilon$ conditions of the waters. This implies two possibilities: (i) natural kinetic
effects prevent mercury species to reach equilibrium in the thermal groundwaters; or,
465 (ii) equilibrium conditions are actually reached but not preserved during sampling,
storage and analysis. For instance, a major part of the measured Hg(II) might be derived
from post-sampling oxidation of Hg_{aq}^0 . At present, we are not able to resolve this
uncertainty and further investigations are thus required..

470 4.3 Mineral-solution equilibrium

The saturation state of the studied groundwaters with respect to some Hg-bearing **minerals**, relevant to ore-formation processes, was also investigated with the PHREEQC code. The most common Hg-minerals associated with epithermal deposits are Cinnabar, Meta-cinnabar and Elemental Mercury ($\text{Hg}_{(l)}$) (Barnes and Seaward, 1997), whose
475 relevant solubility reactions are summarised in Table 2.

The saturation state was evaluated from the saturation index (SI):

$$\text{SI} = \log (\text{IAP}/\text{Kps}) \quad (1)$$

where IAP and Kps are respectively the ionic activity product and the equilibrium constant of the reaction of interest at P and T. For instance, the IAP for the dissolution
480 reaction of Cinnabar is:

$$\log(\text{IAP}) = \log [(a\text{Hg}^{2+}) (a\text{HS}^-)/(a\text{H}^+)] \quad (2)$$

where all activities have been calculated by using the PHREEQC software.

485 The computed SI values are shown in Figure 7a-c. Most of the investigated groundwaters are systematically under-saturated with respect to both HgS and $\text{Hg}_{(l)}$, which supports our earlier statement (cfr. 4.1) of no control of Hg abundance by mineral reactions. The instability of HgS minerals under P-T-X conditions of most studied groundwaters reflects their low Hg content and low-to-moderate sulphur content (see
490 equation in Table 2). Only a few samples characterised by intermediate to high HgD and reducing redox conditions exhibit SI values higher than zero, indicating over-saturation with respect to HgS minerals.

4.4. Hg groundwater budget

495 Determining the mass budget of mercury in volcanic aquifers can permit interesting
comparison with that for aerial volcanic emissions (Bagnato *et al.*, 2007) and provide
useful constraints to evaluating the global source strength of volcanism to Hg
geochemical cycling. Such a determination however requires knowing the bulk
groundwater flow rate in a given volcanic aquifer, which is rarely available or not easy
500 to obtain in most volcanic areas. **As an example**, here we use data for Mount Etna
basaltic volcano whose hydrologic balance is rather well established (Ogniben, 1966;
Aureli, 1973; Ferrara, 1975). Etna's aquifer is recharged by rainwater at an average rate
of 800 mm y⁻¹ over a total surface area of 1200 km². About 75% of this meteoric water
supply actually **infiltrates** into the highly permeable volcanic strata, the complement
505 being evacuated through evapo-transpiration (20%) and surface water run-off (5%).
Ogniben (1966) evaluated a total groundwater discharge of 0.69 km³ y⁻¹ from the
overall volcanic pile. Therefore, combining this value with the mean Hg content of
Etnean groundwaters – whose Hg concentrations are relatively homogenous (Table 1) -
we infer a mean Hg flux of about 14 kg y⁻¹ by aqueous transport. This is several orders
510 of magnitude less than the Hg plume emission rate from the summit craters (**~5x10³ kg**
y⁻¹; Bagnato *et al.*, 2007). Aiuppa *et al.* (2000) made the same observation for other
trace metals (e.g., Cu, Zn, Pb; see Fig. 8), but note the still more prominent release of
Hg in crater emission than from the volcanic aquifer. Such a high prevalence of the
aerial crater emissions of Hg on Etna is consistent with both the high volatility of
515 mercury and the continuous, intense magma degassing activity. The trivial contribution
of aqueous Hg transport to the bulk mercury budget of the volcano has two main
implications: (i) Hg emitted in the volcanic plume suffers little scavenging and
entrainment by rainwater and, thus, has a significant residence time in the atmosphere,
in agreement with its emission and transport as poorly-reactive Hg⁰_(g) (Bagnato *et al.*,
520 2007); and (ii) Both the low Hg content of volcanic rocks and the low temperature

conditions of gas-water-rock interactions in Etna's aquifer contribute to limit the extraction and hydrochemical mobility of Hg during groundwater transport and discharge.

The above observations for Etna may apply to other volcanoes displaying
525 comparable magmatic and degassing activities. But they may not be verified at the much more numerous volcanoes worldwide, including some of those studied here, that display purely hydrothermal activity. At these volcanoes, aqueous transport in volcanic aquifers could represent the prevalent component to their mercury budget. Further studies are **urgently** required to evaluate this aspect.

530

5. Conclusions

Groundwaters from various volcanic aquifers in Italy and Guadeloupe island usually contain low quantities of mercury, from about 10 to 500 ng/l, which are below the
535 WHO concentration threshold of **1000 ng/l** for human health. The variability of Hg concentration in and between the different volcanic aquifers suggests the bearing of complex processes. We find, however, that most of the waters are systematically under-saturated with respect to Hg-bearing condensed phases, thereby supporting the lack of any mineral control on Hg abundance in the conditions of investigated aquifers.
540 Furthermore, we find a positive correlation between total mercury (THg) and dissolved sulfate which strongly suggests that Hg-rich groundwaters receive a direct supply of gaseous elemental mercury ($\text{Hg}^0_{(\text{gas})}$) carried by magmatic/hydrothermal vapours. This offers the perspective that high or increasing mercury content in volcanic aquifers could be a sensitive geochemical tracer of magmatic gas input and, accordingly, could serve to
545 volcano monitoring and eruption forecasting.

Our analytical determinations of mercury speciations demonstrate that a significant proportion of Hg in volcanic waters is transported with the particulate matter. Among the dissolved forms, $\text{Hg}^0_{(\text{aq})}$ and Hg(II) are found to generally occur in almost equal amounts. This analytical observation contrasts with theoretical computations that Hg(II) should be negligible at equilibrium in the groundwater T-pH-pE conditions. Further studies are needed in order to elucidate whether this discrepancy actually reflects unachievement of chemical equilibrium between mercury species in volcanic waters, due to kinetic effects, or whether it is an artefact from sampling/storage procedures that promote the oxidation of $\text{Hg}^0_{(\text{aq})}$ into Hg(II) .

555

Acknowledgements

This study is part of E. Bagnato's PhD Thesis at CFTA Department, Palermo University. Helpful collaboration from the I.N.G.V.-Palermo and the Institute de Physique du Globe de Paris staff, for both logistic support and useful discussions, is acknowledged.

560

6. References

Aiuppa, A., Dongarrà, G., Capasso, G., Allard, P., 2000. Trace element in the thermal groundwaters of Vulcano Island (Sicily). *J. Volcanol. Geoth. Res.* 98, 189-207.

565

Aiuppa, A., Allard, P., D'Alessandro, W., Michel, A., Parello, F., Treuil, M., Valenza, M., 2000. Mobility and fluxes major, minor and trace metals during basalt weathering and groundwater transport at Mt. Etna volcano (Sicily). *Geochim. Cosmochim. Acta* 64, 1827-1841.

570

Aiuppa, A., Allard, P., D'Alessandro, W., Giammanco, S., Parello, F., Valenza, M., 2004. Magmatic gas leakage at Mount Etna (Sicily, Italy): relationships with the volcano-tectonic structures, the hydrological pattern and the eruptive activity. In: "Mt. Etna: Volcano Laboratory". A.G.U. Geophysical Monograph Series 143, 129-145, doi.: 10.1029/143GM09.

575

Aiuppa A., Avino R., Brusca L., Caliro S., Chiodini G., D'Alessandro W., Favara R., Federico C., Ginevra W., Inguaggiato S., Longo M., Pecoraino G., Valenza M., 2006.

- 580 Mineral control of arsenic content in thermal waters from volcano-hosted hydrothermal systems: Insights from island of Ischia and Phlegrean Fields (Campanian Volcanic Province, Italy). *Chem. Geol.* 229, 313–330.
- Allard, P., 1983. The origin of hydrogen, carbon, sulfur, nitrogen and rare gases in volcanic exhalations: evidence from isotope geochemistry. *In: "Forecasting volcanic events"*, Eds. H. Tazieff and J.C. Sabroux, Elsevier, Amsterdam, Chap. 25 : pp. 337-386.
- 585 Allard, P., Carbonnelle, J., Métrich, N., Loyer H., Zettwoog, P., 1994. Sulfur output and magma degassing budget of Stromboli volcano . *Nature* 368, 326-330.
- 590 Allard, P., Jean-Baptiste P., D'Alessandro, W., Parello, F., Parisi, B., and Fleoch, C., 1997. Mantle-derived helium and carbon in groundwaters and gases of Mount Etna, Italy. *Earth Planet. Sci. Lett.* 148, 501-516.
- 595 Allard, P., Aiuppa A., Loyer H., Carrot F., Gaudry, A., Pinte, G., Michel, A., Dongarrà, G., 2000. Acid Gas and Metal Emission Rates during Long-lived Basalt Degassing at Stromboli Volcano. *Geophys. Res. Lett.* 27, no. 8, 1207-1210.
- 600 Allard, P., B. Behncke, S. D'Amico, M. Neri, Gambino S., 2006. Mount Etna 1993–2005: Anatomy of an evolving eruptive cycle. *Earth-Sci. Rev.* 78, 85–114.
- Allard P., Carbonnelle J., Dajlevic D., Le Bronec J., Morel P., Maurenas J.M., Robe M.C., Faivre-Pierret R., Sabroux J.C., Zettwoog P. 1991. Eruptive and diffuse emissions of carbon dioxide from Etna volcano. *Nature*, 351, 387-391.
- 605 Anderson, A., 1979. Mercury in Soils. In: *The Biogeochemistry of Mercury in the Environment*, J.O. Nriagu (ed.). Elsevier, Amsterdam, 79-112.
- 610 Appelo, C.A.J., 1988. WATEQP Program. Institute voor Aard-wetenschappen, **Vrije Universiteit**, Amsterdam.
- Aureli, A., 1973. Idrogeologia del fianco occidentale etneo. *Proceedings of the Second International Symposium on Groundwaters Palermo 28 April–2 May*, 425–487.
- 615 Bagnato, E., Aiuppa, A., Parello, F., Calabrese, S., D'Alessandro, W., Mather, T.A., McGonigle, A.J.S., Pyle, D.M., Wängberg, I. 2007. Degassing of gaseous (elemental and reactive) and particulate mercury from Mount Etna volcano (Southern Italy). *Atmos. Environ.*, 41, 7377-7388.
- 620 Barberi, F., Neri, G., Valenza, M., Villari, L., 1991. 1987-1990 unrest at Vulcano. *Acta Vulcanol.* 1, 95-106.
- Barnes, H.L. and Seaward, T.M., 1997. Geothermal systems and mercury deposits. In: *Geochemistry of Hydrothermal Ore Deposits*. John Wiley & Sons, New York.
- 625 **Bernard, M.L., Molinié, J., Petit, R.H., Beaducel, F., Hammouya, G., Marion, G., 2006. Remote and in situ plume measurements of acid gas release from La Soufrière volcano, Guadeloupe. *J. Volcanol. Geoth. Res.* 150, 395-409.**

- 630 Bloom, N.S., Fitzgerald, W.F., 1988. Determination of volatile mercury species at the picogram level by low-temperature gas chromatography with cold vapour atomic fluorescence detection. *Anal. Chim. Acta* 209, 151-161.
- 635 Boichu, M., Villemant, B., Boudon, G., 2008. A model for episodic degassing of an andesitic magma intrusion. *J. Geophys. Res.*, 113, B07202, doi: 10.1029/2007JB005130.
- 640 Bolognesi, L., and D'Amore, F., 1993. Isotopic variation of the hydrothermal system on Vulcano island, Italy. *Geochim. Cosmochim. Acta* 57, 209-2082.
- 645 Boudon, G., Semet, M., Vincent, P.M., 1989. The evolution of la Grande Decouverte (la Soufriere) volcano, Guadeloupe. F.W.I. in: J. Latter (Ed) *Volcano Hazards : assessment and Monitoring*. IAVCEI Proceedings in Volcanology Vol. 1:86-109, Springer-Verlag.
- 650 Bouysse, P., 1988. Opening of the Grenada back-arc basin and evolution of the Caribbean Plate during the Mesozoic and early Paleogene. *Tectonophysics* 149, 121-143.
- 655 Caliro, S., Panichi, C., Stanzione, D., 1999. Variation in the total dissolved carbon isotope composition of thermal waters of the Island of Ischia (Italy) and its implications for volcanic surveillance. *J. Volcanol. Geoth. Res.* 90, 219-240.
- 660 Caltabiano, T., Burton, M., Giammanco, S., Allard, P., Bruno, N., Murè, F., Romano, R., 2004. Volcanic Gas Emissions From the Summit Craters and Flanks of Mt. Etna, 1987-2000. In: Bonaccorso, A., Calvari, S., Coltelli, M., Del Negro, C., Falsaperla, S. (Eds) 2004. *Etna Volcano Laboratory*. AGU Geophysical Monography Series 143, 111-128.
- 665 Capasso, G., D'Alessandro, W., Favara, R., Inguaggiato, S., Parello, F., 2001. Interaction between the deep fluids and the shallow groundwaters on Vulcano island (Italy). *J. Volcanol. Geoth. Res.* 108, no.1, 187-198(12).
- 670 Carapezza, M.L., Federico, C., 2000. The contribution of fluid geochemistry to the volcano monitoring of Stromboli. *J. Volcanol. Geoth. Res.* 95, 227-245.
- 675 Chiodini, G., Allard, P., Caliro, S., Parello, F., 2000. ^{18}O exchange between steam and carbon dioxide in volcanic and hydrothermal gases: implications for the origin of water. *Geochim. Cosmochim. Acta*, Vol. 64, 14, 2479-2488.
- Christenson, B.W., Mroczek, E. K., 2003. Potential Reaction Pathways of Hg in Some New Zealand Hydrothermal Environments. *Society of Economic Geologists* 10, 111-132.
- Civetta, L., Cornette, Y., Crisci, G., Gillot, P. Y., Orsi, G. and C. S. Requejo, 1984. Geology, geochronology and chemical evolution of the island of Pantelleria. *Geological Magazine*, vol. 121; N°. 6, 541-562.

- 680 D'Alessandro, W., Dongarrà G., Guerrieri, S., Parello, F., Valenza, M., 1994. Geochemical characterization of naturally occurring fluids on Island of Pantelleria (Italy). *Miner. Petrogr. Acta* 37, 91-102.
- Ferrara, V., *Idrogeologia del versante orientale dell'Etna*, in: *Proc. of the 3rd Intern. Conf. on Groundwaters*, 91-144, 1975.
- 685 Fitzgerald, W. F., 1986. Cycling of mercury between the atmosphere and oceans. In: Buat-Menard, P. (Ed.), *The Role of Air-Sea Exchange in Geochemical Cycling*, NATO Advanced Institute Series. Reidel, Dordrecht, The Netherlands, 363-408.
- 690 Fitzgerald, W. F., Lamborg, C.H., 2003. Geochemistry of mercury in the environment. In: Sherwood Lollar, B. (Ed.), *Treatise on Geochemistry* vol. 9, 107-148.
- Fleischer, M., 1970. Procedures of the International Mineralogical Association Commission on New Minerals and Mineral Names. *American Mineralogist* 55, 1016-1017.
- 695 Fulignati, G., Malfitano, A., Sbrana, A., 1997. The Pantelleria caldera geothermal system: data from the hydrothermal minerals. *J. Volcanol. Geoth. Res.* 75, 251-270.
- 700 Gauthier, P.J., Le Cloarec, M.F., 1998. Variability of alkali and heavy metal fluxes released by Mt. Etna volcano, Sicily, between 1991 and 1995. *J. Volcanol. Geoth. Res.* 81, 311-326.
- Giggenbach, W. F., 1988. Geothermal solute equilibria. Derivation of Na-K-Mg-Ca geoindicators. *Geochim. Cosmochim. Acta* 52, 2749-2763.
- 705 Herdianita, N.R., Priadi, B., 2008. Arsenic and Mercury Concentrations at Several Geothermal Systems in West Java, Indonesia. *J. Sci.*, vol. 40, N°. 1, 1-14.
- 710 Hornig-Kjarsgaard, I., Keller, J., Koberski, U., Stadlbauer, E., Francalanci, L., Lenhart, R., 1993. Geology, stratigraphy and volcanological evolution of the island of Stromboli, Aeolian arc, Italy. *Acta Vulcanol.* 3, 21-68
- Horvat, M., Kotnik, J., Logar, M., Fajon, V., Zvonaric, T., Pirrone, N., 2003. Speciation of mercury in surface and deep-sea waters in the Mediterranean Sea. *Atmos. Environ.* 37, Supplement No. 1, S93-S108.
- 715 HSC 1999, HSC chemistry for Windows, Version 4, Outokumpu Research Oy, pori, Finland.
- 720 Ikingura, J.R., Akagi, H., 1999. Methylmercury production and distribution in aquatic systems. *Sci. Total Environ.* 234, 109-118.
- Inguaggiato, S., Rizzo, A., 2004. Dissolved helium isotope ratios in groundwaters: a new technique based on gas-water re-equilibration and its application to Stromboli volcanic system. *Appl. Geochem.* 19, 665-673.
- 725 Jenne, E.A., 1970. Atmospheric and fluvial transport of mercury. In: *Mercury in the Environment*. Geological Survey profession 713, 40-45.

- 730 Khodakovskii, I.L., Shikina, N.D., 1981. The role of carbonate complexes in mercury transport in hydrothermal solutions (experimental studies and thermodynamic analysis). *Geochem. Int.* 18, 32-43.
- 735 Komorowski, J.C., Boudon, G., Antenor-Habazac, C., Hammouya, G., Semet, M., J. David, Beauducel, Cheminée, J.L., Feuillard, M., 2001. L'activité éruptive et non-éruptive de la Soufrière de Guadeloupe: problèmes et implications de la phénoménologie et des signaux actuellement enregistrés, INSU Lesser Antilles Volcanic Hazard Workshop, Paris, pp. 18–21, abstract volume.
- 740 Lee, Y. H., Iverfeldt, A., 1991. Measurement of methylmercury and mercury in run-off, lake and rain waters. *Water, Air and Soil Pollution* 56, 405-414.
- 745 Lin. C.-J., Pehkonen, S.O., 1999a. The chemistry of atmospheric mercury: a review. *Atmos. Environ.* 33, 2067-2079.
- Lin. C.-J., Pehkonen, S.O., 1999b. Aqueous phase reactions of mercury with free radicals and chlorine: Implications for atmospheric mercury chemistry. *Chemosphere* 38, no.6, 1253-1263.
- 750 Lindqvist, O., Rodhe, H., 1985. Atmospheric mercury – a review. *Tellus* 27B, 136-159.
- Mason, R. P., Fitzgerald, W. F., Morel, F.M.M., 1994. The biogeochemical cycling of elemental mercury: Anthropogenic influences. *Geochim. Cosmochim. Acta* 58 (15), 3191-3198.
- 755 Nriagu, J., Becker, C., 2003. Volcanic emissions of mercury to the atmosphere: global and regional inventories. *Sci. Total Environ.* 304, 3-12.
- 760 Ogniben, L., 1966. Lineamenti idrogeologici dell'Etna, *Rivista Mineraria Siciliana*, 100-102, 1-24.
- Paonita, A., Favara, R., Nuccio, P.M., Sortino, F., 2002. Genesis of fumarolic emissions as inferred by isotope mass balances: CO₂ and water at Vulcano Island, Italy. *Geochim. Cosmochim. Acta* 66, 759-772
- 765 Parello, F., Allard, P., D'Alessandro, W., Federico, C., Jean-Baptiste, P., Catani, O., 2000. Isotope geochemistry of Pantelleria volcanic fluids, Sicily Channel rift: a mantle volatile end-member for volcanism in southern Europe. *Earth Planet. Sc. Lett.* 180 325-339
- 770 Parker, J.L., Bloom, N.S., 2005. Preservation and storage techniques for low-level aqueous mercury speciation. *Sci. Total Environ.* 337, 253-263.
- 775 Parkhurst, D.L., 1995. User's guide to PHEEQC—A computer program for speciation, reaction-path, advective-transport, and inverse geochemical calculations. U.S. Geological Survey Water-Resources Investigations report 143, 95-4227.
- 780 Pyle, D.M., Mather, A.M., 2003. The importance of volcanic emissions for the global atmospheric mercury cycle. *Atmos. Environ.* 37, 5115-5124.

- Sarkar, D., Essington, M.E., Mishra, K.C., 2000. Adsorption of Mercury (II) by Kaolinite. *Soil Sci.Soc. Am.J.* 64, 1968-1975.
- 785 Siegel, S.M., Siegel, B.Z., 1984. First estimate of annual mercury flux at Kilauea main vent. *Nature* 309, 146-147.
- Slemr, F., Schuster, G., Seiler, W., 1985. Distribution, speciation and budget of atmospheric mercury. *Atmos. Environ.* 3, 407-434.
- 790 Stumm, W., Morgan, J. J. (Eds), 1996. *Aquatic Chemistry- Chemical Equilibria and Rates in Natural Waters*, 3rd Edition. Wiley Interscience, New York.
- TEKRAN, 1998. Model 2600.-principles of operations. <http://tekran.com>
- 795 U.S. E.P.A (1999) Method 1631: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapour Atomic Fluorescence Spectrometry". Washington (DC): Office of Water, Engineering.
- 800 Varekamp, J. C., Buseck, P.R., 1984. The speciation of mercury in hydrothermal systems, with applications for ore deposition. *Geochim. Cosmochim. Acta* 48, 177-186.
- Varekamp, J. C., Buseck, P.R., 1986. Global mercury flux from volcanic and geothermal sources. *Appl. Geochem.* 1, 65-73.
- 805 Villemant, B., Boudon, G., 1999. H₂O and halogens (F, Cl, Br) behaviour during shallow magma degassing processes. *Earth Planet. Sc. Lett.* 168, Issue 3-4, 271-286.
- Villemant, B., Hammouya, G., Michel, A., Semet, M.P., Komorowski, J.C., Boudon, G., Cheminee, J.L., 2005. The memory of volcanic waters: Shallow magma degassing revealed by halogen monitoring in thermal springs of La Soufriere volcano (Guadeloupe, Lesser Antilles). *Earth Planet. Sci. Lett.*, doi: 10.1016/j.epsl.2005.05.013.
- Washington, H.S., 1909. The submarine eruptions of 1831 and 1891 near Pantelleria. *Am. J. Sci.* 27, 131-150.
- 815 Watras, C.J., Bloom, N.S., Hudson, R.J.M., Gherini, S., Munson, R., Claas, S.A., Morrison, K.A., Hurley, J., Wiener, J.G., Fitzgerald, W.F., Mason, R., Vandal, G., Powell, D., Rada, R., Rislov, L., Winfrey, M., Elder, J., Krabbenhoft, D., Andren, A.W., Babiarz, C., Porcella, D.B., and Huckabee, J.W., 1994. Sources and fates of mercury and methylmercury in Wisconsin lakes". In: *Mercury Pollution : Integration and Synthesis*, (eds. C. Watras and J. Huckabee, chapter I.12). Lewis Publishers, Ann Arbor, MI, 153-177.
- 820 7. WHO (1993): WHO Guidelines for Drinking Water Quality-
http://www.who.int/water_sanitation_health/GDWQ/index.html. **Captions of**

Tables and Figures

Table 1 – Main chemical composition (mg/l) and concentrations of mercury species
 830 (ng/l) in the studied volcanic groundwaters of Italy (Etna, Stromboli, Vulcano,
 Pantelleria and Ischia) and Guadeloupe (La Soufrière volcano, Lesser Antilles). TDS =
 Total Dissolved Solids (mg/l).

Table 2 – Hg-minerals and their solubility reactions.

835

Fig. 1 – Location map of the investigated volcanoes: **(a) Mt. Etna; (b) Stromboli island; (c) Vulcano island; (d) Pantelleria island; (e) Ischia island; and (f) La Soufrière** (Guadeloupe island, Lesser Antilles).

840 **Fig. 2** – Triangular plots for major cations (a) and anions (b) in the analysed groundwaters.

Fig. 3 – Total mercury (THg)-SO₄ scatter diagram for the investigated volcanic aquifers. Note the positive co-variation of THg with sulphate concentration displayed by actively
 845 degassing volcanoes such as Stromboli, Vulcano, Ischia and Guadeloupe.

Fig. 4 – THg-pH scatter diagram for the analysed volcanic waters.

A clear dependency of THg on pH is observed: groundwaters with acid to neutral pH values (from 4.9 to 7) are systematically richer in THg (>100 ng/l), whereas neutral to
 850 basic groundwaters (pH from 7 to 9.11) always contain less than 65 ng/l of THg .

Fig. 5 – Distribution of analytically determined Hg speciation forms in the investigated groundwaters: (a) THg vs Hg_D, (b) Hg_p vs Hg_D, and (c) Hg(II) vs Hg⁰_{aq}.

Diagrams show: (a) a general co-variation of Hg_D and THg concentrations; (b)
 855 particulate mercury (Hg_p) makes an important fraction of THg (50% on average), even

though the HgD/HgP ratio is highly variable (0.05 to 56); and (c) a greater stability of Hg_{aq}^0 over $Hg(II)$ among the aqueous forms of mercury.

Fig. 6 – Computed theoretical distribution of mercury speciation forms within the
860 volcanic aquifers at thermodynamic equilibrium. . .

Logarithmic molar concentrations, calculated with the PHREEQC software and updated thermodynamic data for Hg-bearing aqueous species, are plotted against the corresponding $p\epsilon$ (a) and chlorine content (b) of the waters. The results indicate that: (i) Hg_{aq}^0 is the main aqueous form of mercury in all the investigated groundwaters. The
865 concentrations of $Hg(II)$ species increase with $p\epsilon$ values, but should be several orders of magnitude lower than Hg_{aq}^0 even in oxidizing conditions; and (ii) there is no particular dependency of Hg_{aq}^0 on groundwater chlorine content.

Fig. 7 – Saturation Index of the investigated groundwaters with respect to Hg-bearing
870 mineral phases (a) Cinnabar, (b) Metacinnabar (b) and (c) $Hg_{(l)}$, in function of pH of the solution.

All but a few of the investigated volcanic waters are under-saturated with respect to both HgS and $Hg_{(l)}$ forms.

875 **Fig. 8** – Mass budget for aqueous transport of mercury (grey square) and other trace metals at Etna, compared to corresponding crater plume emissions (yearly averaged values). Data sources: *Aiuppa et al.* (2004), *Bagnato et al.* (2007) and this study. Atmosphere elements (open circles), volatile and lithophile species (open squares) are also distinguished in the plot.

880 Note how the volcanic aquifer discharge contributes minor mercury (14 kg y^{-1}), compared to plume emissions ($5 \times 10^3 \text{ kg y}^{-1}$), to the overall budget of this very active basaltic volcano in continuous magmatic activity. See text for discussion.

Mercury concentration, speciation and budget in volcanic aquifers: Italy and Guadeloupe (Lesser Antilles)

E. Bagnato^{1,*}, A. Aiuppa^{1,2}, F. Parelo¹, W. D'Alessandro²,

5 P. Allard³, S. Calabrese¹

¹Dipartimento CFTA, Università di Palermo, Via Archirafi 36, 90123 Palermo, Italy

²INGV, Sezione di Palermo, Via La malfa 153, Palermo, Italy

³Laboratoire Pierre Sue, CNRS-CEA, CE-Saclay, 91191 Gif/Yvette, France

10

*Corresponding author. Tel.: +39091611574; fax: +390916168376

E-mail address: e.bagnato@unipa.it (E. Bagnato)

Abstract – Quantifying the contribution of volcanism to global mercury (Hg) emissions
15 is important to understand the pathways and the mechanisms of Hg cycling through the
Earth's geochemical reservoirs and to assess its environmental impacts. While previous
studies have suggested that degassing volcanoes might contribute importantly to the
atmospheric budget of mercury, little is known about the amount and behaviour of Hg
in volcanic aquifers. Here we report on detailed investigations of both the content and
20 the speciation of mercury in aquifers of active volcanoes in Italy and Guadeloupe Island
(Lesser Antilles). In the studied groundwaters, total Hg (THg) concentrations range
from 10 to 500 ng/l and are lower than the 1000 ng/l threshold value for human health
protection fixed by the World Health Organization (WHO, 1993). Positive co-variations
of (THg) with sulphate indicate that Hg-SO₄-rich acid groundwaters receive a direct
25 input of magmatic/hydrothermal gases carrying mercury as Hg⁰_(gas). Increasing THg in a
volcanic aquifer could thus be a sensitive tracer of magmatic gas input prior to an
eruption. Since the complex behaviour and toxicity of mercury in waters depend on its

chemical speciation, we carefully determined the different aqueous forms of this element in our samples. We find that dissolved elemental $\text{Hg}^0_{(\text{aq})}$ and particulate-bound Hg (Hg_p) widely prevail in volcanic aquifers, in proportions that highlight the efficiency of Hg adsorption onto colloidal particles. Moreover, we observe that dissolved Hg^0_{aq} and Hg(II) forms coexist in comparable amount in most of the waters, in stark contrast to the results of thermodynamic equilibrium modelling. Therefore, chemical equilibrium between dissolved mercury species in volcanic waters is either prevented by natural kinetic effects or not preserved in collected waters due to sampling/storage artefacts. Finally, we provide a first quantitative comparison of the relative intensity of aqueous transport and atmospheric emissions of mercury at Mount Etna, a very active basaltic volcano.

Keywords: *speciation, volcanic aquifers, total and dissolved mercury, mercury cycling, volatile budget*

40

1. Introduction

Volcanic degassing represents an important natural source of various toxic elements to the atmosphere and shallow aqueous systems (e.g. Pyle and Mather, 2003). Groundwaters circulating in active volcanic areas may contain appreciable amounts of trace metals as a result of their direct interaction with magma-derived fluids, the leaching of host volcanic rocks by gas-rich acid waters, or the leaching of ore deposits. The study of volcanic aquifers provides insights into the cycling of trace elements along various steps of the hydrological cycle, including the infiltration of meteoric waters into permeable volcanic layers, their interaction with rocks and uprising magmatic volatiles in a reducing and acid environment, and the final discharge to the surface. Furthermore, the determination of potentially harmful elements in volcanic aquifers is crucial because these often constitute an important water resource for local communities.

55 Mercury is one of these harmful elements. It is a highly volatile and toxic trace metal
that is released into the hydrosphere, atmosphere and biosphere through both
anthropogenic and natural processes, the latter including degassing from active
volcanoes (Siegel and Siegel, 1984; Fitzgerald, 1986; Mason *et al.*, 1994; Pyle and
Mather, 2003). In the atmosphere, mercury is transported in its volatile (elemental
60 gaseous mercury Hg^0), reactive (Hg(II)) and particulate-bound (Hg_p) forms (Lin and
Pehkonen, 1999a,b; Lindqvist and Rodhe, 1985). In the marine and terrestrial
environments, inorganic Hg is often methylated to methylmercury species which readily
accumulate in marine organisms (Slemr *et al.*, 1985; Fitzgerald *et al.*, 1986, 2003; Lee
and Iverfeldt, 1991). In groundwater environments, mercury is known to bio-
65 accumulate and to become very dangerous to human health when exceeding threshold
concentrations in drinking water (Nriagu and Becker, 2003; Ikingura and Akagi, 1999).
The toxicity of this element strongly depends on its chemical form and, owing to its
complex geochemical behaviour, determining its speciation in groundwaters requires
appropriate techniques for sampling and preservation of aqueous samples (Parker and
70 Bloom, 2005). Analysis of Hg species in water can be made by studying the mercury
distribution between total, dissolved and particulate-bound forms within an aquifer
system. Since mercury often occurs at very low concentrations in natural waters, serious
problems can often arise from sampling and post-sampling procedures, due to possible
losses or contamination during storage.

75 The mercury speciation in volcanic groundwaters is still poorly characterised, and
very few data exist for the mercury content in hydrothermal systems (Varekamp and
Buseck, 1986; Christenson and Mroczek; 2003). Therefore, our objective in this study
has been to determine both the concentration and the speciation of mercury contained in
selected volcanic aquifers, in order to improve our current understanding of Hg hydro-
80 cycling in volcanic environments. Using the analytical procedures established by Parker

and Bloom (2005), we measured the concentrations of total (THg), dissolved (HgD) and particulate (Hg_p) mercury in water samples from volcanic aquifers located in Southern Italy (Mt. Etna, Sicily, and Vulcano, Stromboli, Ischia and Pantelleria volcanic islands) and the Lesser Antilles (Soufriere volcano, Guadeloupe island). We also provide a new
85 estimate of the proportions of [Hg(II)] and Hg⁰_{aq} species among the dissolved forms of mercury in volcanic aquifers. Finally, we quantitatively assess the mass budget of aqueous transport of mercury at Mount Etna and its contribution to the bulk Hg budget of that very active basaltic volcano.

90 2. Studied sites and methods

2.1 Studied sites

The volcanoes of Southern Italy and Guadeloupe whose aquifers we studied are all actively degassing. They are representative of different volcanic activity level, ranging
95 from open conduit degassing with frequent eruptions at Etna and Stromboli to quiescent hydrothermal manifestations at Vulcano, Pantelleria, Ischia and La Soufrière. These volcanoes are fed by different magma types (from basalt to andesite) and are located in distinct geodynamic contexts (tensional fracturing or rifting for Etna and Pantelleria, subduction zones for all other ones). Below we summarize the main features of these
100 different volcanic sites:

(a) Mt. Etna is a very active and large (40 km wide, 3.3 km high) alkali basaltic strato-
volcano, that has built since 0.6 Ma on tensional tectonic faults on the Eastern coast of Sicily (Fig. 1). It produces frequent summit and flank eruptions (e.g. Allard *et al.*, 2006) and continuously releases huge amounts of magmatic volatiles from its summit craters,
105 which makes it one of the strongest volcanic emitters of many volatile species with potential environmental impact (Allard *et al.*, 1991; Gauthier and Le Cloarec 1998;

Caltabiano *et al.*, 2004). Its groundwater system is extensive and has been the subject of several chemical and isotopic studies (see Aiuppa *et al.*, 2004, and references therein).

(b) Stromboli is the most active volcano of the Quaternary Aeolian island arc, north of Sicily (Fig. 1), beneath which the Ionian oceanic plate is still subducting. It is a 3 km high, prevalently submarine basaltic strato-volcano whose upper part, Stromboli island (3-4 km in diameter, 924 m high), emerges from the Tyrrhenian sea. Its feeding magmas have a calc-alkaline to shoshonitic affinity and range in age from approximately 0.2 Ma to present (Hornig-Kjarsgaard *et al.* 1993). Quiescent and explosive gas emissions from Stromboli craters are approximately one order of magnitude lower than those from Mt. Etna, but are representative of erupting arc volcanoes (Allard *et al.*, 1994, 2000). Thermal waters (~40°C) diluted by sea water occur along its southeastern coast.

(c) Vulcano island is located in the southern-central part of the Aeolian Arc (Fig. 1). Since its last explosive (vulcanian) eruption, in 1888–1890, its active cone (La Fossa) has continued to be the site of intense fumarolic activity. Intermittent periods of increasing fumarole temperatures (up to 700°C) and spatial extension, connected with seismic activity, occurred in the 1920s then between 1978 to the present day (Barberi *et al.* 1991; Paonita *et al.* 2002). The composition of the fumarolic gases results from the mixing of magmatic gas with hydrothermal and seawater-derived fluids (Paonita *et al.* 2002; Chiodini *et al.*, 2000). A very active hydrothermal system, tapped by wells or manifested by thermal springs, surrounds the active volcanic cone.

(d) Pantelleria volcanic island (83 km², 836 m a.s.l.) is located 100 km SW of Sicily and 70 km off the Tunisian coast (Fig.1), on the axis of the Sicily Channel tensional rift zone. This large strato-volcano, topped with a caldera, is quiescent at present but six eruptive cycles have been recognized in the last 50 ka at Pantelleria (Civetta *et al.*, 1984). Its most recent eruption was submarine and happened 3 km NW of the island in October-December 1891 (Washington, 1909). Widespread thermal manifestations on

Pantelleria attest to a sustained heat flow and have been the subject of a few previous studies (Parello *et al.*, 2000). Many hot springs and thermal wells (30-81°C) are distributed in the NE and SW sectors of the island, most of which lie along the coastline.

(e) Ischia is the westernmost active volcanic complex of the Campania area and belongs to the Phlegrean volcanic district, which also includes Campi Flegrei and Procida (Fig.1). Many thermal manifestations and modest seismic activity characterize the current activity of the island (Caliro *et al.*, 1999). Thermal waters, submarine and subaerial fumaroles are well known since Roman times and still constitute an important touristic and economic resource for the island.

(f) Finally, Guadeloupe island, located on the eastern margin of the Caribbean plate (Bouysse, 1988) (Fig.1), belongs to the intra-oceanic Lesser Antilles volcanic arc..Its currently active volcano, La Soufrière, is an andesitic complex with lava domes and cones. Since its last magmatic eruption in 1530 (Komorowski *et al.*, 2001), La Soufrière volcano has maintained a very intense hydrothermal activity punctuated by a series of violent phreatic eruptions (Boudon *et al.*, 1989; Komorowsky *et al.*, 2001). At present, strong fumarolic degassing, generating plume emissions (Bernard *et al.*, 2006), occur from the summit of the lava dome and numerous thermal springs are distributed within 0.5-5 km distance around the lava dome. Historical observations showed that the nature, distribution, and intensity of these geothermal manifestations have fluctuated considerably over time and He-carbon isotopic measurements demonstrate a magmatic origin of the gases (Allard, 1983; Allard *et al.*, 2000).

155

2.2. Sampling and analytical methods

Twenty-two water samples were collected at Mt Etna (springs, wells and drainage galleries), 9 samples on Vulcano (wells), 27 thermal waters on Ischia (wells and

springs), two (thermal water wells) on Stromboli, 10 samples on Pantelleria (wells and
160 springs) and 9 thermal springs around Soufriere volcano in Guadeloupe.

In order to avoid mercury contamination, waters were collected and stored in
completely fully filled glass bottles with Teflon-lined caps that were pre-cleaned in
laboratory by soaking them with a 10% HNO₃ solution for about 48 hours, then rinsed
several times with Hg-free MilliQ water and dried in a class 100 fume hood (Bloom *et*
165 *al.*, 1988). One bottle blank was always analyzed for each batch in order to check the
cleaning procedure. During sample collection, bottles were rinsed three times in the
field with sampling water before being filled.

General water quality parameters (pH, Eh, T, Electric Conductivity) were measured
in the field with portable instruments. Major element analysis (Na, K, Mg, Ca, Cl, NO₃
170 and SO₄) was made at INGV-Pa by Ionic Chromatography while total Alkalinity was
determined by titration with HCl 0.1M. The chemical composition of the investigated
volcanic groundwaters is reported in Table 1.

Total mercury analysis was made on unfiltered water, while samples for the
determination of dissolved Hg were filtered through 0,20 µm filters. Both were acidified
175 with 0,4% (v/v) ultra-pure HCl and stored refrigerated in the dark. Total and dissolved
mercury were analysed at C.F.T.A. Dept. in Palermo using BrCl oxidation, SnCl₂
reduction, dual amalgamation, and cold vapour atomic fluorescence spectrometry
(CVAFS), according to the U.S.EPA Method 1631 (Bloom *et al.*, 1988). A Tekran 2600
analyzer with gold quartz-sand traps was used for pre-concentrating mercury. Our
180 detection limit (MDL) is 0.5 ng l⁻¹ and the analytical reproducibility is ±10%.

Divalent ionic mercury [Hg(II)], was determined by analyzing fresh, un-acidified and
un-oxidized water samples that were reduced with SnCl₂ by means of the same
apparatus (Parker and Bloom, 2005). The Hg analyzer was calibrated using a five-point
calibration curve, and inorganic Hg standards were prepared by direct dilution of NIST-

185 certified 10,000-ppm aqueous Hg standard solution. Particulate mercury content in
waters (Hg_p) was estimated as the difference between the measured total and dissolved
mercury concentrations, according to EPA 1631 method procedure. The results are
given in Table 1.

190 **3. Results**

3.1 Groundwaters chemistry

On Mt. Etna, water samples were collected at different elevations and distributed
over an area of about 1200 km². The sampled waters are characterised by low
195 temperatures (mean about 16°C) and pH values ranging from 6.07 to 7.56. Previous
isotopic studies (Allard *et al.*, 1997; D'Alessandro *et al.*, 2004) have demonstrated the
meteoric origin of Etnean groundwaters. The chemical composition of Mt. Etna
groundwaters is strongly controlled by the dissolution of magma-derived CO₂ in the
aquifer, which in turn promotes intense acid leaching of the host basaltic rocks. This
200 process, which takes place in a cold environment, is responsible for the typical
bicarbonate-alkaline to alkaline-earth chemical composition of groundwaters in the
volcano's aquifers (Fig. 2a,b). The amount of metals that are released into the
groundwaters depends on the intensity of the water-rock interaction processes inside the
aquifer (Aiuppa *et al.*, 2000).

205 The two thermal waters sampled on Stromboli Island (Fulco and Zurro wells) have
temperatures of 42° and 36°C and pHs of 6.36 and 7.00, respectively. Both samples
have a Na-Cl composition (Fig. 2a,b) and are interpreted as mixtures of bicarbonate-rich
meteoric water and seawater (TDS between 17,500 and 18,800 mg/l) (Carapezza and
Federico, 1999). Their high HCO₃ content (between 253 and 652 mg/l) reflects the input

210 of magmatic-derived CO₂, as evidenced by the isotopic ratios of dissolved CO₂ and He
(Inguaggiato *et al.*, 2004).

The sampled groundwaters on Vulcano Island have temperatures ranging from 22° to
61°C and pH values between 6.36 and 7.8. They display a wide compositional range,
from sulphate-chloride-alkaline to sulphate-chloride-earth-alkaline waters (Fig. 2a,b).
215 The origin of their high contents in either Cl or SO₄ remains a matter of debate
(Bolognesi and D'Amore, 1993; Capasso *et al.* 2001): NaCl groundwaters (Castello,
EAS) are attributed to either sea-water intrusion in the Vulcano Porto area (Fig. 2a,b) or
the ascent of NaCl hydrothermal brines (Bolognesi and D'Amore, 1993). Sulphate-rich
groundwaters are instead interpreted as being meteoric waters steam-heated by H₂S-rich
220 hydrothermal fluids, boiled off from the reservoirs at depth (Aiuppa *et al.* 2000;
Capasso *et al.* 2001).

The chemistry of Pantelleria's thermal waters is mainly dominated by a mixing
process between meteoric water and seawater-dominated thermal waters, a process that
gives rise to chloride-alkaline compositions (Fig. 2a,b). The thermal waters were shown
225 to derive from a large hydrothermal system reaching about 250°C at 1.5-2 km depth
(D'Alessandro *et al.*, 1994; Fulignati *et al.*, 1997). The collected water samples
represent partially-equilibrated fluids (Giggenbach, 1988), with Na-K equilibrium
temperatures of 180 to 200 °C. Highly concentrated NaHCO₃-rich solutions with high
pH (8.44-9.25) occur in Specchio di Venere Lake, an endoreic basin.

230 Thermal waters from Ischia island have contrasting compositions, from bicarbonate-
rich (HCO₃ from 171 to 2110 mg/l) to chloride-rich (Cl from 91 to 19000 mg/l) (Fig.
2a,b). The bicarbonate waters are representative of local meteoric groundwaters variably
heated by interaction with CO₂-rich vapours of deep origin. These waters exhibit
temperatures from 28 to 67 °C, TDS from 1270 to 4420 mg/l, and pCO₂ values from 2.3
235 to 6.3 atm. Chloride-rich groundwaters are characterized by temperatures of 26 to 91

°C, have high TDS (max value 38200 mg/l) and Na as the main cation. These fluids represent mixtures of meteoric water and sea water that are variably heated and chemically modified at depth within the hydrothermal system (Aiuppa *et al.*, 2006).

At La Soufrière volcano, the distribution of thermal springs around the summit lava dome is controlled by the topography of the basement and the occurrence of argillitic hydrothermal alteration zones. The collected waters are characterized by temperatures from 21° to 58°C and pH values between 4.93 and 6.43. Our and previous data indicate that Ca-SO₄ waters (Fig. 2a-b) prevail close to the lava dome (Bain Jaunes, Carbet l'Echelle, Galion and Matouba). These steam-heated waters result from the interactions of meteoric groundwater with CO₂-H₂S-rich vapour of magmatic origin, whose condensation gives rise to highest HCO₃⁻ and SO₄²⁻ contents in the most proximal spring of Carbet l'Echelle. Instead, Ca-Na-HCO₃ waters (Habitation Revel) correspond to shallow groundwaters that interact with a cold CO₂-rich magmatic gas phase. Finally, Ca-Na-Cl waters (Chutes du Carbet) are interpreted as a mixture between Ca-SO₄ waters and Na-Cl waters (Villemant *et al.*, 2005). The lack of systematic correlations between halogens (Cl, Br, and F) and cation contents indicate that seawater contribution can be ruled out. Previous studies ascribed the excess of halogens to a mixing process between meteoric water and a true magmatic component that transports Cl⁻ and Br⁻ ions from a deep gas source to the shallow aquifers (Boichu *et al.*, 2008; Villemant *et al.*, 1999).

3.2. Mercury content in groundwaters

The total Hg content of all analysed groundwaters cover a wide range from about 10 to 500 ng/l (Table1). Such concentrations are below the threshold value of 1000 ng/l that was set by the World Health Organization (WHO) for human health protection. The abundances of mercury in natural waters depend on many factors such as temperature,

pH, the highly volatile nature of the element, and its tendency to be adsorbed onto clays, iron and manganese hydroxides and organic matter (Jenne, 1970). The simultaneous action of these factors, combined with the low abundance of mercury in crustal rocks (10⁻⁶-10⁻⁴ wt%; Fleisher, 1970), account for the very low and variable mercury concentrations often exhibited by natural waters. We explore thereafter the influence of these factors on the mercury content and speciation in our volcanic water samples.

3.2.1. Mt. Etna

Etna's groundwaters have a variable but generally low mercury content (Table 1), with THg values ranging from 4 to 34 ng/l and averaging ~14 ng/l. HgD content averages 8 ng/l (range 1.5-25) and particulate mercury (Hg_p) 7 ng/l (range 2.5-28). The latter accounts for about 50% of THg, while Hg⁰_{aq} represents the main aqueous species (60 to 100% of HgD). These relatively high proportions of Hg⁰_{aq} probably reflect the reduced conditions (low pO₂) of the waters (Varekamp and Buseck, 1984). The overall low mercury content of Etnean groundwaters is consistent with their low temperatures (10-20°C) and negligible extraction of Hg from the aquifer rocks during low-temperature underground water-rock interactions. In contrast, the hypothermal brines discharged at "Salinelle" display higher mercury contents, with THg and HgD concentrations of 112 ng/l and 74 ng/l, respectively. Particulate Hg content was evaluated as about 38 ng/l, while Hg⁰_{aq} content is 53 ng/l. The higher concentrations of mercury in these brines can be related to both their reduced conditions (Eh = -17 mV), high chloride content (Cl = 41200 mg/l), and the higher equilibrium temperature (T~140°C) estimated for their feeding hydrothermal reservoir. In fact, the formation of Hg-Cl complexes in saline waters (Khodakovskii *et al.*, 1981) enhances Hg aqueous transport.

3.2.2. *Stromboli*

The two thermal water wells, Zurro (35°C) and Fulco (41°C), we sampled on
290 Stromboli island have slightly-acidic pH, reducing redox potentials and high SO₄
contents (1200 and 1400 mg/l, respectively). Their concentrations in mercury are much
higher than those generally found in Etna groundwaters (Table 1), with mean THg and
HgD values reaching 195 and 33 ng/l, respectively. Hg(II) species amount to 3.8 and
18.4 ng/l and particulate Hg_p (182 and 141 ng/l) prevails over the dissolved Hg forms,
295 which points to a prevalent transport of mercury in the suspended colloidal phase in
these thermal waters.

3.2.3. *Vulcano*

Vulcano groundwaters display average THg and HgD concentrations of 45 ng/l
300 (range 11-139) and 6.6 ng/l (range 2.7-18.4), that are intermediate between those for
Etna and Stromboli (Table 1). THg correlates positively with SO₄ (Fig. 3) and
negatively with the water redox potential; the highest THg content (139 ng/l) is detected
in Castello sample that is also among the richest in SO₄ (1680 mg/l) and the more
reducing ones (Eh = - 250 mV). Quite high THg are also found in Discarica (77 ng/l)
305 and Bartolo (65 ng/l) SO₄-rich waters, which are also characterised by reducing and
acidic conditions. Most of the mercury present in Vulcano groundwaters occurs as
Hg(P): this latter averages about 38 ng/l (range 3.4-133) and is the most concentrated in
Castello (133 ng/l), Discarica (75 ng/l) and Bartolo (54 ng/l) waters. Particulate mercury
(Hg_p) contributes the complement to the highest measured total Hg contents. In most
310 waters Hg(II) is the main dissolved species, accounting for 40 to 100% of HgD and
averaging 5.6 ng/l (range 3-10). Again, the larger proportion of the Castello sample
stands out for its much larger proportion of Hg⁰_{aq} (about 60% of HgD), in agreement
with its more reducing conditions (Table 1).

315 3.2.4. *Pantelleria*

On Pantelleria island thermal waters have modest THg concentrations (average: 22 ng/l, range from 12 to 47 ng/l), and a mean dissolved mercury (HgD) content of about 10 ng/l (range 2-15) (Table 1). The highest THg values are found at Buvira Rizzo (47 ng/l) and in the Specchio di Venere lake (41 ng/l) within and around which intense gas
320 manifestations do exist. Particulate mercury Hg_p contributes quite variable proportions of THg (range: 0.5 to 45 ng/l, and mean: 12 ng/l; Table 1). Hg(II) varies from 2 to 9 ng/l (mean: 5), while Hg^0_{aq} ranges from 0.16 to 10 ng/l (mean: 4).

3.2.5. *Ischia*

325 Ischia thermal waters exhibit a great variability in Hg content, in agreement with the wide temperature and compositional range of the waters constituting the aquifer (Table 1 and Fig. 2a,b). THg vary from 1.1 to 205 ng/l (mean: 45 ng/l) and HgD from 0.9 to 169 ng/l (mean: 22 ng/l). Particulate mercury represents a minor proportion of THg (mean: 21 ng/l, range: 0.5-113 ng/l) when comparing to other volcanic aquifers. Among
330 the dissolved species, Hg^0_{aq} (range 1.8 - 39 ng/l, mean 14 ng/l) is the most abundant one. Hg(II) contents vary from 1.6 to 153 ng/l (mean: 12.5 ng/l).

3.2.6. *La Soufriere volcano (Guadeloupe)*

Thermal springs surrounding La Soufrière lava dome are the richest in mercury
335 among all the waters analysed in this study (Table 1). Their THg and HgD contents respectively average 230 ng/l (range: 10 to 494) and 133 ng/l (range: 9 to 247). Hg_p varies from 1 to 358 ng/l (mean: 137 ng/l) and accounts for 10 to 90% of total mercury. Hg^0_{aq} (4.2 to 296 ng/l, mean: 125 ng/l) is generally the main aqueous Hg species, Hg(II) contents averaging only 8 ng/l. At La Soufrière there is a clear negative dependency of

340 THg on pH (Fig. 4). The most acidic (pH <6) groundwaters, issuing at the base of the
lava dome (Carbet l'Echelle, Ravine Marchand, Pas du Roy, Bains jaunes and Galion),
are typically the most enriched in mercury (Table 1). These waters are also the richest in
sulfate and display low redox conditions (Eh between -100 and 100 mV) and low TDS
content (366 to 2683 mg/l). Therefore, as already suggested for Vulcano waters, the
345 positive correlation between THg and SO₄ (Fig. 3) in La Soufriere thermal waters
supports the idea of that most of the mercury is directly supplied as Hg⁰ by CO₂-H₂S-
rich vapours of magmatic origin that condense in the aquifers while reacting with
groundwater.

350 4. Discussion

4.1 Factors and processes controlling the abundance of Hg in volcanic aquifers

Mercury can be supplied to volcanic groundwaters by several processes, such as
direct input of Hg-bearing fluids of magmatic origin, the raise of Hg-rich hydrothermal
355 steam boiled-off by hydrothermal brines at depth, and water-rock interactions in hot and
acid hydrothermal aquifers. At the surface and in groundwaters, Hg availability is a
complex function of many factors: total concentration and “speciation” of the metal
itself, mineralogy of the host rocks, pH, redox potential, temperature, total organic
content, suspended particulate abundance and aquifer discharge rate (Watras *et al.*,
360 1994; Sarkar *et al.*, 2000). Such a complex behaviour of mercury in hydrothermal-
volcanic environments is clearly reflected in its wide concentration variations in thermal
waters analysed in this study (Tab. 1) and previously (Varekamp and Buseck, 1984;
Christenson *et al.*, 2003; Herdianita and Priadi, 2008).

No first order cause-effect relationship can explain the extreme variability, by several
365 orders of magnitude, of mercury concentrations in the studied volcanic aquifers. First,

the measured total (THg) and dissolved (HgD) mercury concentrations are independent on the groundwater discharge temperature. Since solubilities of Hg-S minerals and Hg_(l) are positively correlated with temperature (Varekamp and Buseck, 1984), the lack of systematic Hg-temperature correlation argues against a control of Hg aqueous contents

370 by any mineral-solution equilibrium process in the studied aquifers. On the other hand, a peculiar dependency of THg on groundwater pH is observed (Fig. 4): groundwaters with THg > 100 ng/l are systematically characterised by acid to neutral pH values (from 4.9 to 7), while THg concentrations in neutral to basic environments (pH from 7 to 9.11) are typically < 65 ng/l. Two main factors may account for this observation:

375 (i) Groundwater pH is the main factor controlling Hg adsorption onto mineral surfaces. It has been demonstrated (Anderson, 1979) that surface adsorption of mercury is minor at low pH values, but favoured in alkaline oxidised environments. Owing to the very high affinity of mercury for adsorption onto clay minerals and iron oxy-hydroxides, which are among the main secondary phases formed by low-temperature weathering of

380 volcanic rocks (Aiuppa *et al.*, 2000), heterogeneous surface reactions could be a determining factor in controlling Hg hydrocycling in volcanic aquifers.

(ii) In a volcanic aquifer, groundwater pH is determined by the amount and rate of dissolution of reactive and acidic gases, such as CO₂, SO₂, H₂S and HCl, and by the extent of water-rock interaction. In general, low pH and p_e values are typical of the

385 initial stages of gas-water-rock interaction, during which the dissolution of acid magmatic/hydrothermal gases in groundwater promotes intense and isochemical leaching of the host-rocks (Giggenbach, 1988). With increasing extent of gas-water-rock interaction, pH and p_e values tend to increase due to their buffering by rock dissolution and interaction with atmospheric gases. Accordingly, it can be argued that

390 high Hg contents in volcanic waters may date to the pristine stages of gas-water-rock interaction, during which mercury originally transported as volatile Hg⁰_{gas} (Varekamp

and Buseck, 1984) is primarily provided by condensation of magmatic/ hydrothermal vapours. This process can prevail as long as the input of deep fluids is maintained and fresh (un-altered) volcanic rocks remain available. Along with more extensive
395 interaction with the host rocks (e.g., when groundwater residence time in the aquifer is long enough or when reactive gases become less abundant), oxidizing and basic environments are gradually formed, promoting Hg^0 oxidation to Hg(II) and thus the scavenging of Hg adsorbed onto mineral surfaces. Groundwaters studied here are in most (all) cases representative of the shallowest parts of hydrothermal systems.
400 Therefore, they are most-likely to dissolve/react with a low-T volcanic gas phase, which has previously been interacting (upon its ascent with deeper hydrothermal reservoir(s)) In such circumstances, the low-T volcanic gas phase will have H_2S as its main S species (with SO_2 being scrubbed from and being converted to H_2S).

The positive correlation between THg and SO_4 depicted in Figure 3 provides strong
405 evidence that aqueous Hg is generally contributed from a Hg-rich gas precursor. In fact, this correlation is especially clear at volcanic sites such as Vulcano, Stromboli and La Soufriere, where continuous supply of magmatic heat and magma-derived volatiles directly sustains intense fumarolic discharge and hydrothermal circulation. At these volcanoes, high sulphate contents in thermal waters are systematically associated with
410 low pH and Eh, and therefore are consistent with groundwater heating by condensation of H_2S -bearing hydrothermal steam, followed by H_2S oxidation by atmospheric gases (Giggenbach, 1988). Hence, the co-variation of THg and sulphate in these “steam-heated groundwaters” strengthens our conclusion that Hg-rich volcanic waters result from a direct feeding by magmatic/hydrothermal vapours. We suggest that Hg is mainly
415 contributed to the aquifer as Hg^0_{vap} , transported by the uprising CO_2 and H_2S -rich geothermal/magmatic steam. Upon interaction with the aquifer, Hg^0_{vap} is dissolved as Hg^0 , and partially oxidised to Hg(II) aqueous forms due to the oxidizing conditions of

shallow groundwaters. A non-negligible part of the oxidized Hg forms can eventually be adsorbed onto the particulate (colloidal) phase.

420

4.2 Mercury speciation in volcanic waters: experimental and model evidences

The measured speciations of mercury in our water sample set provide important constraints on the partitioning of this element between its various ionic and particulate forms. The results of analytically-determined Hg speciation are summarised in Figure 425 5a-c. Figure 5a demonstrates a positive correlation between THg and HgD concentrations, the former prevailing over the latter, which validates the reliability of our analytical procedures. This correlation also implies that particulate-bound mercury (Hg_p), calculated as the difference between THg and HgD, constitutes an important fraction of THg, averaging about 50% (Fig. 5b). The HgD/Hg_p ratio however displays a 430 great variability from 0.05 to 56 (Fig. 5b). Samples from Vulcano are systematically enriched in Hg_p, whereas the opposite is observed on Pantelleria and Ischia: there, HgD generally exceeds Hg_p, likely because the high TDS and Cl contents of these groundwaters (Table 1) enlarge the stability field of dissolved forms such as HgCl₂.

Our results also provide new insight into the relative abundances of the dissolved 435 forms (Hg⁰_{aq} and Hg(II)) of mercury. Figure 5c demonstrates a great variability in the proportions of these two dissolved forms, even though they occur in nearly equal amount on average. To summarise, the following conclusions can be derived from our experimental determinations of Hg speciation:

- (i) Dissolved and particulate forms are typically present in equal amounts in the 440 studied groundwaters, highlighting the important role played by adsorption processes on colloidal particle surfaces;
- (ii) Dissolved Hg⁰_{aq} and Hg(II) forms also occur in comparable amounts in most of the investigated groundwaters, but display large variations in some other waters.

The experimentally-determined Hg speciations discussed above can be compared
445 with theoretical equilibrium activities of dissolved Hg in groundwaters under the
measured T, pH, and $p\epsilon$ conditions, computed by using the PHREEQC speciation
software (Parkhurst, 1995). Such a comparison allows us to check whether Hg species
either reach or not thermodynamic equilibrium in the aqueous phase. For these
computations, we used a modified version of the WATEQP thermochemical database
450 (Appelo, 1988), implemented with thermochemical data from the HSC database (HSC,
1999) for the most relevant aqueous and condensed Hg species. Figure 6a shows the
computed equilibrium molar concentrations of Hg_{aq}^0 and Hg(II) for the investigated
groundwaters, as calculated with PHREEQC, versus the corresponding redox potential
(given by groundwater $p\epsilon$). The diagram indicates that Hg_{aq}^0 should be the main
455 equilibrium Hg aqueous form in all studied waters (molar abundance $\sim 10^{-10}$), as also
inferred for some thermal waters in New Zealand (Christenson et al., 2003). Hg(II)
increases with increasing $p\epsilon$ values, but remain several orders of magnitude lower than
 Hg_{aq}^0 at equilibrium, even in oxidizing conditions (range: 10^{-34} to 10^{-14} M). HgCl_2
prevails among the Hg(II) species, depending on the water Cl content (Fig. 6b).

460 Comparison between Figures 5c and 6a clearly demonstrates that our analytical
results are in stark contrast with the computed equilibrium speciations: the relative
proportions of measured Hg(II) are far larger than those expected at equilibrium in the
T, pH, $p\epsilon$ conditions of the waters. This implies two possibilities: (i) natural kinetic
effects prevent mercury species to reach equilibrium in the thermal groundwaters; or,
465 (ii) equilibrium conditions are actually reached but not preserved during sampling,
storage and analysis. For instance, a major part of the measured Hg(II) might be derived
from post-sampling oxidation of Hg_{aq}^0 . At present, we are not able to resolve this
uncertainty and further investigations are thus required..

470 4.3 Mineral-solution equilibrium

The saturation state of the studied groundwaters with respect to some Hg-bearing minerals, relevant to ore-formation processes, was also investigated with the PHREEQC code. The most common Hg-minerals associated with epithermal deposits are Cinnabar, Meta-cinnabar and Elemental Mercury ($\text{Hg}_{(l)}$) (Barnes and Seaward, 1997), whose
 475 relevant solubility reactions are summarised in Table 2.

The saturation state was evaluated from the saturation index (SI):

$$\text{SI} = \log (\text{IAP}/\text{Kps}) \quad (1)$$

where IAP and Kps are respectively the ionic activity product and the equilibrium constant of the reaction of interest at P and T. For instance, the IAP for the dissolution
 480 reaction of Cinnabar is:

$$\log(\text{IAP}) = \log [(a\text{Hg}^{2+}) (a\text{HS}^-)/(a\text{H}^+)] \quad (2)$$

where all activities have been calculated by using the PHREEQC software.

485 The computed SI values are shown in Figure 7a-c. Most of the investigated groundwaters are systematically under-saturated with respect to both HgS and $\text{Hg}_{(l)}$, which supports our earlier statement (cfr. 4.1) of no control of Hg abundance by mineral reactions. The instability of HgS minerals under P-T-X conditions of most studied groundwaters reflects their low Hg content and low-to-moderate sulphur content (see
 490 equation in Table 2). Only a few samples characterised by intermediate to high HgD and reducing redox conditions exhibit SI values higher than zero, indicating over-saturation with respect to HgS minerals.

4.4. Hg groundwater budget

495 Determining the mass budget of mercury in volcanic aquifers can permit interesting
comparison with that for aerial volcanic emissions (Bagnato *et al.*, 2007) and provide
useful constraints to evaluating the global source strength of volcanism to Hg
geochemical cycling. Such a determination however requires knowing the bulk
groundwater flow rate in a given volcanic aquifer, which is rarely available or not easy
500 to obtain in most volcanic areas. As an example, here we use data for Mount Etna
basaltic volcano whose hydrologic balance is rather well established (Ogniben, 1966;
Aureli, 1973; Ferrara, 1975). Etna's aquifer is recharged by rainwater at an average rate
of 800 mm y⁻¹ over a total surface area of 1200 km². About 75% of this meteoric water
supply actually infiltrates into the highly permeable volcanic strata, the complement
505 being evacuated through evapo-transpiration (20%) and surface water run-off (5%).
Ogniben (1966) evaluated a total groundwater discharge of 0.69 km³ y⁻¹ from the
overall volcanic pile. Therefore, combining this value with the mean Hg content of
Etnean groundwaters – whose Hg concentrations are relatively homogenous (Table 1) -
we infer a mean Hg flux of about 14 kg y⁻¹ by aqueous transport. This is several orders
510 of magnitude less than the Hg plume emission rate from the summit craters (~**5x10³ kg**
y⁻¹; Bagnato *et al.*, 2007). Aiuppa *et al.* (2000) made the same observation for other
trace metals (e.g., Cu, Zn, Pb; see Fig. 8), but note the still more prominent release of
Hg in crater emission than from the volcanic aquifer. Such a high prevalence of the
aerial crater emissions of Hg on Etna is consistent with both the high volatility of
515 mercury and the continuous, intense magma degassing activity. The trivial contribution
of aqueous Hg transport to the bulk mercury budget of the volcano has two main
implications: (i) Hg emitted in the volcanic plume suffers little scavenging and
entrainment by rainwater and, thus, has a significant residence time in the atmosphere,
in agreement with its emission and transport as poorly-reactive Hg⁰_(g) (Bagnato *et al.*,
520 2007); and (ii) Both the low Hg content of volcanic rocks and the low temperature

conditions of gas-water-rock interactions in Etna's aquifer contribute to limit the extraction and hydrochemical mobility of Hg during groundwater transport and discharge.

The above observations for Etna may apply to other volcanoes displaying
525 comparable magmatic and degassing activities. But they may not be verified at the much more numerous volcanoes worldwide, including some of those studied here, that display purely hydrothermal activity. At these volcanoes, aqueous transport in volcanic aquifers could represent the prevalent component to their mercury budget. Further studies are urgently required to evaluate this aspect.

530

5. Conclusions

Groundwaters from various volcanic aquifers in Italy and Guadeloupe island usually contain low quantities of mercury, from about 10 to 500 ng/l, which are below the
535 WHO concentration threshold of 1000 ng/l for human health. The variability of Hg concentration in and between the different volcanic aquifers suggests the bearing of complex processes. We find, however, that most of the waters are systematically under-saturated with respect to Hg-bearing condensed phases, thereby supporting the lack of any mineral control on Hg abundance in the conditions of investigated aquifers.
540 Furthermore, we find a positive correlation between total mercury (THg) and dissolved sulfate which strongly suggests that Hg-rich groundwaters receive a direct supply of gaseous elemental mercury ($\text{Hg}^0_{(\text{gas})}$) carried by magmatic/hydrothermal vapours. This offers the perspective that high or increasing mercury content in volcanic aquifers could be a sensitive geochemical tracer of magmatic gas input and, accordingly, could serve to
545 volcano monitoring and eruption forecasting.

Our analytical determinations of mercury speciations demonstrate that a significant proportion of Hg in volcanic waters is transported with the particulate matter. Among the dissolved forms, $\text{Hg}^0_{(\text{aq})}$ and $\text{Hg}(\text{II})$ are found to generally occur in almost equal amounts. This analytical observation contrasts with theoretical computations that $\text{Hg}(\text{II})$ should be negligible at equilibrium in the groundwater T-pH-pE conditions. Further studies are needed in order to elucidate whether this discrepancy actually reflects unachievement of chemical equilibrium between mercury species in volcanic waters, due to kinetic effects, or whether it is an artefact from sampling/storage procedures that promote the oxidation of $\text{Hg}^0_{(\text{aq})}$ into $\text{Hg}(\text{II})$.

555

Acknowledgements

This study is part of E. Bagnato's PhD Thesis at CFTA Department, Palermo University. Helpful collaboration from the I.N.G.V.-Palermo and the Institute de Physique du Globe de Paris staff, for both logistic support and useful discussions, is acknowledged.

560

6. References

Aiuppa, A., Dongarrà, G., Capasso, G., Allard, P., 2000. Trace element in the thermal groundwaters of Vulcano Island (Sicily). *J. Volcanol. Geoth. Res.* 98, 189-207.

565

Aiuppa, A., Allard, P., D'Alessandro, W., Michel, A., Parello, F., Treuil, M., Valenza, M., 2000. Mobility and fluxes major, minor and trace metals during basalt weathering and groundwater transport at Mt. Etna volcano (Sicily). *Geochim. Cosmochim. Acta* 64, 1827-1841.

570

Aiuppa, A., Allard, P., D'Alessandro, W., Giammanco, S., Parello, F., Valenza, M., 2004. Magmatic gas leakage at Mount Etna (Sicily, Italy): relationships with the volcano-tectonic structures, the hydrological pattern and the eruptive activity. In: "Mt. Etna: Volcano Laboratory". A.G.U. Geophysical Monograph Series 143, 129-145, doi.: 10.1029/143GM09.

575

Aiuppa A., Avino R., Brusca L., Caliro S., Chiodini G., D'Alessandro W., Favara R., Federico C., Ginevra W., Inguaggiato S., Longo M., Pecoraino G., Valenza M., 2006.

- 580 Mineral control of arsenic content in thermal waters from volcano-hosted hydrothermal systems: Insights from island of Ischia and Phlegrean Fields (Campanian Volcanic Province, Italy). *Chem. Geol.* 229, 313–330.
- Allard, P., 1983. The origin of hydrogen, carbon, sulfur, nitrogen and rare gases in volcanic exhalations: evidence from isotope geochemistry. *In: "Forecasting volcanic events"*, Eds. H. Tazieff and J.C. Sabroux, Elsevier, Amsterdam, Chap. 25 : pp. 337-386.
- 585 Allard, P., Carbonnelle, J., Métrich, N., Loyer H., Zettwoog, P., 1994. Sulfur output and magma degassing budget of Stromboli volcano . *Nature* 368, 326-330.
- 590 Allard, P., Jean-Baptiste P., D'Alessandro, W., Parello, F., Parisi, B., and Fleoch, C., 1997. Mantle-derived helium and carbon in groundwaters and gases of Mount Etna, Italy. *Earth Planet. Sci. Lett.* 148, 501-516.
- 595 Allard, P., Aiuppa A., Loyer H., Carrot F., Gaudry, A., Pinte, G., Michel, A., Dongarrà, G., 2000. Acid Gas and Metal Emission Rates during Long-lived Basalt Degassing at Stromboli Volcano. *Geophys. Res. Lett.* 27, no. 8, 1207-1210.
- 600 Allard, P., B. Behncke, S. D'Amico, M. Neri, Gambino S., 2006. Mount Etna 1993–2005: Anatomy of an evolving eruptive cycle. *Earth-Sci. Rev.* 78, 85–114.
- Allard P., Carbonnelle J., Dajlevic D., Le Bronec J., Morel P., Maurenas J.M., Robe M.C., Faivre-Pierret R., Sabroux J.C., Zettwoog P. 1991. Eruptive and diffuse emissions of carbon dioxide from Etna volcano. *Nature*, 351, 387-391.
- 605 Anderson, A., 1979. Mercury in Soils. In: *The Biogeochemistry of Mercury in the Environment*, J.O. Nriagu (ed.). Elsevier, Amsterdam, 79-112.
- 610 Appelo, C.A.J., 1988. WATEQP Program. Institute voor Aard-wetenschappen, Vrije Universiteit, Amsterdam.
- Aureli, A., 1973. Idrogeologia del fianco occidentale etneo. *Proceedings of the Second International Symposium on Groundwaters Palermo 28 April–2 May*, 425–487.
- 615 Bagnato, E., Aiuppa, A., Parello, F., Calabrese, S., D'Alessandro, W., Mather, T.A., McGonigle, A.J.S., Pyle, D.M., Wängberg, I. 2007. Degassing of gaseous (elemental and reactive) and particulate mercury from Mount Etna volcano (Southern Italy). *Atmos. Environ.*, 41, 7377-7388.
- 620 Barberi, F., Neri, G., Valenza, M., Villari, L., 1991. 1987-1990 unrest at Vulcano. *Acta Vulcanol.* 1, 95-106.
- Barnes, H.L. and Seaward, T.M., 1997. Geothermal systems and mercury deposits. In: *Geochemistry of Hydrothermal Ore Deposits*. John Wiley & Sons, New York.
- 625 Bernard, M.L., Molinié, J., Petit, R.H., Beaducel, F., Hammouya, G., Marion, G., 2006. Remote and in situ plume measurements of acid gas release from La Soufrière volcano, Guadeloupe. *J. Volcanol. Geoth. Res.* 150, 395-409.

- 630 Bloom, N.S., Fitzgerald, W.F., 1988. Determination of volatile mercury species at the picogram level by low-temperature gas chromatography with cold vapour atomic fluorescence detection. *Anal. Chim. Acta* 209, 151-161.
- 635 Boichu, M., Villemant, B., Boudon, G., 2008. A model for episodic degassing of an andesitic magma intrusion. *J. Geophys. Res.*, 113, B07202, doi: 10.1029/2007JB005130.
- 640 Bolognesi, L., and D'Amore, F., 1993. Isotopic variation of the hydrothermal system on Vulcano island, Italy. *Geochim. Cosmochim. Acta* 57, 209-2082.
- 645 Boudon, G., Semet, M., Vincent, P.M., 1989. The evolution of la Grande Decouverte (la Soufriere) volcano, Guadeloupe. F.W.I. in: J. Latter (Ed) *Volcano Hazards : assessment and Monitoring*. IAVCEI Proceedings in Volcanology Vol. 1:86-109, Springer-Verlag.
- 650 Bouysse, P., 1988. Opening of the Grenada back-arc basin and evolution of the Caribbean Plate during the Mesozoic and early Paleogene. *Tectonophysics* 149, 121-143.
- 655 Caliro, S., Panichi, C., Stanzione, D., 1999. Variation in the total dissolved carbon isotope composition of thermal waters of the Island of Ischia (Italy) and its implications for volcanic surveillance. *J. Volcanol. Geoth. Res.* 90, 219-240.
- 660 Caltabiano, T., Burton, M., Giammanco, S., Allard, P., Bruno, N., Murè, F., Romano, R., 2004. Volcanic Gas Emissions From the Summit Craters and Flanks of Mt. Etna, 1987-2000. In: Bonaccorso, A., Calvari, S., Coltelli, M., Del Negro, C., Falsaperla, S. (Eds) 2004. *Etna Volcano Laboratory*. AGU Geophysical Monography Series 143, 111-128.
- 665 Capasso, G., D'Alessandro, W., Favara, R., Inguaggiato, S., Parello, F., 2001. Interaction between the deep fluids and the shallow groundwaters on Vulcano island (Italy). *J. Volcanol. Geoth. Res.* 108, no.1, 187-198(12).
- 670 Carapezza, M.L., Federico, C., 2000. The contribution of fluid geochemistry to the volcano monitoring of Stromboli. *J. Volcanol. Geoth. Res.* 95, 227-245.
- 675 Chiodini, G., Allard, P., Caliro, S., Parello, F., 2000. ^{18}O exchange between steam and carbon dioxide in volcanic and hydrothermal gases: implications for the origin of water. *Geochim. Cosmochim. Acta*, Vol. 64, 14, 2479-2488.
- Christenson, B.W., Mroczek, E. K., 2003. Potential Reaction Pathways of Hg in Some New Zealand Hydrothermal Environments. *Society of Economic Geologists* 10, 111-132.
- Civetta, L., Cornette, Y., Crisci, G., Gillot, P. Y., Orsi, G. and C. S. Requejo, 1984. Geology, geochronology and chemical evolution of the island of Pantelleria. *Geological Magazine*, vol. 121; N°. 6, 541-562.

- 680 D'Alessandro, W., Dongarrà G., Guerrieri, S., Parello, F., Valenza, M., 1994. Geochemical characterization of naturally occurring fluids on Island of Pantelleria (Italy). *Miner. Petrogr. Acta* 37, 91-102.
- Ferrara, V., *Idrogeologia del versante orientale dell'Etna*, in: *Proc. of the 3rd Intern. Conf. on Groundwaters*, 91-144, 1975.
- 685 Fitzgerald, W. F., 1986. Cycling of mercury between the atmosphere and oceans. In: Buat-Menard, P. (Ed.), *The Role of Air-Sea Exchange in Geochemical Cycling*, NATO Advanced Institute Series. Reidel, Dordrecht, The Netherlands, 363-408.
- 690 Fitzgerald, W. F., Lamborg, C.H., 2003. Geochemistry of mercury in the environment. In: Sherwood Lollar, B. (Ed.), *Treatise on Geochemistry* vol. 9, 107-148.
- Fleischer, M., 1970. Procedures of the International Mineralogical Association Commission on New Minerals and Mineral Names. *American Mineralogist* 55, 1016-1017.
- 695 Fulignati, G., Malfitano, A., Sbrana, A., 1997. The Pantelleria caldera geothermal system: data from the hydrothermal minerals. *J. Volcanol. Geoth. Res.* 75, 251-270.
- 700 Gauthier, P.J., Le Cloarec, M.F., 1998. Variability of alkali and heavy metal fluxes released by Mt. Etna volcano, Sicily, between 1991 and 1995. *J. Volcanol. Geoth. Res.* 81, 311-326.
- Giggenbach, W. F., 1988. Geothermal solute equilibria. Derivation of Na-K-Mg-Ca geoindicators. *Geochim. Cosmochim. Acta* 52, 2749-2763.
- 705 Herdianita, N.R., Priadi, B., 2008. Arsenic and Mercury Concentrations at Several Geothermal Systems in West Java, Indonesia. *J. Sci.*, vol. 40, N°. 1, 1-14.
- 710 Hornig-Kjarsgaard, I., Keller, J., Koberski, U., Stadlbauer, E., Francalanci, L., Lenhart, R., 1993. Geology, stratigraphy and volcanological evolution of the island of Stromboli, Aeolian arc, Italy. *Acta Vulcanol.* 3, 21-68
- Horvat, M., Kotnik, J., Logar, M., Fajon, V., Zvonaric, T., Pirrone, N., 2003. Speciation of mercury in surface and deep-sea waters in the Mediterranean Sea. *Atmos. Environ.* 37, Supplement No. 1, S93-S108.
- 715 HSC 1999, HSC chemistry for Windows, Version 4, Outokumpu Research Oy, pori, Finland.
- 720 Ikingura, J.R., Akagi, H., 1999. Methylmercury production and distribution in aquatic systems. *Sci. Total Environ.* 234, 109-118.
- Inguaggiato, S., Rizzo, A., 2004. Dissolved helium isotope ratios in groundwaters: a new technique based on gas-water re-equilibration and its application to Stromboli volcanic system. *Appl. Geochem.* 19, 665-673.
- 725 Jenne, E.A., 1970. Atmospheric and fluvial transport of mercury. In: *Mercury in the Environment*. Geological Survey profession 713, 40-45.

- 730 Khodakovskii, I.L., Shikina, N.D., 1981. The role of carbonate complexes in mercury transport in hydrothermal solutions (experimental studies and thermodynamic analysis). *Geochem. Int.* 18, 32-43.
- 735 Komorowski, J.C., Boudon, G., Antenor-Habazac, C., Hammouya, G., Semet, M., J. David, Beauducel, Cheminée, J.L., Feuillard, M., 2001. L'activité éruptive et non-éruptive de la Soufrière de Guadeloupe: problèmes et implications de la phénoménologie et des signaux actuellement enregistrés, INSU Lesser Antilles Volcanic Hazard Workshop, Paris, pp. 18–21, abstract volume.
- 740 Lee, Y. H., Iverfeldt, A., 1991. Measurement of methylmercury and mercury in run-off, lake and rain waters. *Water, Air and Soil Pollution* 56, 405-414.
- 745 Lin. C.-J., Pehkonen, S.O., 1999a. The chemistry of atmospheric mercury: a review. *Atmos. Environ.* 33, 2067-2079.
- Lin. C.-J., Pehkonen, S.O., 1999b. Aqueous phase reactions of mercury with free radicals and chlorine: Implications for atmospheric mercury chemistry. *Chemosphere* 38, no.6, 1253-1263.
- 750 Lindqvist, O., Rodhe, H., 1985. Atmospheric mercury – a review. *Tellus* 27B, 136-159.
- Mason, R. P., Fitzgerald, W. F., Morel, F.M.M., 1994. The biogeochemical cycling of elemental mercury: Anthropogenic influences. *Geochim. Cosmochim. Acta* 58 (15), 3191-3198.
- 755 Nriagu, J., Becker, C., 2003. Volcanic emissions of mercury to the atmosphere: global and regional inventories. *Sci. Total Environ.* 304, 3-12.
- 760 Ogniben, L., 1966. Lineamenti idrogeologici dell'Etna, *Rivista Mineraria Siciliana*, 100-102, 1-24.
- Paonita, A., Favara, R., Nuccio, P.M., Sortino, F., 2002. Genesis of fumarolic emissions as inferred by isotope mass balances: CO₂ and water at Vulcano Island, Italy. *Geochim. Cosmochim. Acta* 66, 759-772
- 765 Parello, F., Allard, P., D'Alessandro, W., Federico, C., Jean-Baptiste, P., Catani, O., 2000. Isotope geochemistry of Pantelleria volcanic fluids, Sicily Channel rift: a mantle volatile end-member for volcanism in southern Europe. *Earth Planet. Sc. Lett.* 180 325-339
- 770 Parker, J.L., Bloom, N.S., 2005. Preservation and storage techniques for low-level aqueous mercury speciation. *Sci. Total Environ.* 337, 253-263.
- 775 Parkhurst, D.L., 1995. User's guide to PHEEQC—A computer program for speciation, reaction-path, advective-transport, and inverse geochemical calculations. U.S. Geological Survey Water-Resources Investigations report 143, 95-4227.
- 780 Pyle, D.M., Mather, A.M., 2003. The importance of volcanic emissions for the global atmospheric mercury cycle. *Atmos. Environ.* 37, 5115-5124.

- Sarkar, D., Essington, M.E., Mishra, K.C., 2000. Adsorption of Mercury (II) by Kaolinite. *Soil Sci.Soc. Am.J.* 64, 1968-1975.
- 785 Siegel, S.M., Siegel, B.Z., 1984. First estimate of annual mercury flux at Kilauea main vent. *Nature* 309, 146-147.
- Slemr, F., Schuster, G., Seiler, W., 1985. Distribution, speciation and budget of atmospheric mercury. *Atmos. Environ.* 3, 407-434.
- 790 Stumm, W., Morgan, J. J. (Eds), 1996. *Aquatic Chemistry- Chemical Equilibria and Rates in Natural Waters*, 3rd Edition. Wiley Interscience, New York.
- TEKRAN, 1998. Model 2600.-principles of operations. <http://tekran.com>
- 795 U.S. E.P.A (1999) Method 1631: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapour Atomic Fluorescence Spectrometry". Washington (DC): Office of Water, Engineering.
- 800 Varekamp, J. C., Buseck, P.R., 1984. The speciation of mercury in hydrothermal systems, with applications for ore deposition. *Geochim. Cosmochim. Acta* 48, 177-186.
- Varekamp, J. C., Buseck, P.R., 1986. Global mercury flux from volcanic and geothermal sources. *Appl. Geochem.* 1, 65-73.
- 805 Villemant, B., Boudon, G., 1999. H₂O and halogens (F, Cl, Br) behaviour during shallow magma degassing processes. *Earth Planet. Sc. Lett.* 168, Issue 3-4, 271-286.
- Villemant, B., Hammouya, G., Michel, A., Semet, M.P., Komorowski, J.C., Boudon, G., Cheminee, J.L., 2005. The memory of volcanic waters: Shallow magma degassing revealed by halogen monitoring in thermal springs of La Soufriere volcano (Guadeloupe, Lesser Antilles). *Earth Planet. Sci. Lett.*, doi: 10.1016/j.epsl.2005.05.013.
- Washington, H.S., 1909. The submarine eruptions of 1831 and 1891 near Pantelleria. *Am. J. Sci.* 27, 131-150.
- 815 Watras, C.J., Bloom, N.S., Hudson, R.J.M., Gherini, S., Munson, R., Claas, S.A., Morrison, K.A., Hurley, J., Wiener, J.G., Fitzgerald, W.F., Mason, R., Vandal, G., Powell, D., Rada, R., Rislov, L., Winfrey, M., Elder, J., Krabbenhoft, D., Andren, A.W., Babiarz, C., Porcella, D.B., and Huckabee, J.W., 1994. Sources and fates of mercury and methylmercury in Wisconsin lakes". In: *Mercury Pollution : Integration and Synthesis*, (eds. C. Watras and J. Huckabee, chapter I.12). Lewis Publishers, Ann Arbor, MI, 153-177.
- 820 7. WHO (1993): WHO Guidelines for Drinking Water Quality-
http://www.who.int/water_sanitation_health/GDWQ/index.html. **Captions of**

Tables and Figures

Table 1 – Main chemical composition (mg/l) and concentrations of mercury species
 830 (ng/l) in the studied volcanic groundwaters of Italy (Etna, Stromboli, Vulcano,
 Pantelleria and Ischia) and Guadeloupe (La Soufrière volcano, Lesser Antilles). TDS =
 Total Dissolved Solids (mg/l).

Table 2 – Hg-minerals and their solubility reactions.

835

Fig. 1 – Location map of the investigated volcanoes: **(a) Mt. Etna; (b) Stromboli island; (c) Vulcano island; (d) Pantelleria island; (e) Ischia island; and (f) La Soufrière** (Guadeloupe island, Lesser Antilles).

840 **Fig. 2** – Triangular plots for major cations (a) and anions (b) in the analysed groundwaters.

Fig. 3 – Total mercury (THg)-SO₄ scatter diagram for the investigated volcanic aquifers. Note the positive co-variation of THg with sulphate concentration displayed by actively
 845 degassing volcanoes such as Stromboli, Vulcano, Ischia and Guadeloupe.

Fig. 4 – THg-pH scatter diagram for the analysed volcanic waters.

A clear dependency of THg on pH is observed: groundwaters with acid to neutral pH values (from 4.9 to 7) are systematically richer in THg (>100 ng/l), whereas neutral to
 850 basic groundwaters (pH from 7 to 9.11) always contain less than 65 ng/l of THg .

Fig. 5 – Distribution of analytically determined Hg speciation forms in the investigated groundwaters: (a) THg vs Hg_D, (b) Hg_p vs Hg_D, and (c) Hg(II) vs Hg⁰_{aq}.

Diagrams show: (a) a general co-variation of Hg_D and THg concentrations; (b)
 855 particulate mercury (Hg_p) makes an important fraction of THg (50% on average), even

though the HgD/HgP ratio is highly variable (0.05 to 56); and (c) a greater stability of Hg_{aq}^0 over $Hg(II)$ among the aqueous forms of mercury.

Fig. 6 – Computed theoretical distribution of mercury speciation forms within the
860 volcanic aquifers at thermodynamic equilibrium. . .

Logarithmic molar concentrations, calculated with the PHREEQC software and updated thermodynamic data for Hg-bearing aqueous species, are plotted against the corresponding $p\epsilon$ (a) and chlorine content (b) of the waters. The results indicate that: (i) Hg_{aq}^0 is the main aqueous form of mercury in all the investigated groundwaters. The
865 concentrations of $Hg(II)$ species increase with $p\epsilon$ values, but should be several orders of magnitude lower than Hg_{aq}^0 even in oxidizing conditions; and (ii) there is no particular dependency of Hg_{aq}^0 on groundwater chlorine content.

Fig. 7 – Saturation Index of the investigated groundwaters with respect to Hg-bearing
870 mineral phases (a) Cinnabar, (b) Metacinnabar (b) and (c) $Hg_{(l)}$, in function of pH of the solution.

All but a few of the investigated volcanic waters are under-saturated with respect to both HgS and $Hg_{(l)}$ forms.

875 **Fig. 8** – Mass budget for aqueous transport of mercury (grey square) and other trace metals at Etna, compared to corresponding crater plume emissions (yearly averaged values). Data sources: *Aiuppa et al.* (2004), *Bagnato et al.* (2007) and this study. Atmosphere elements (open circles), volatile and lithophile species (open squares) are also distinguished in the plot.

880 Note how the volcanic aquifer discharge contributes minor mercury (14 kg y^{-1}), compared to plume emissions ($5 \times 10^3 \text{ kg y}^{-1}$), to the overall budget of this very active basaltic volcano in continuous magmatic activity. See text for discussion.

Figure1

[Click here to download Figure: Fig 1.pdf](#)

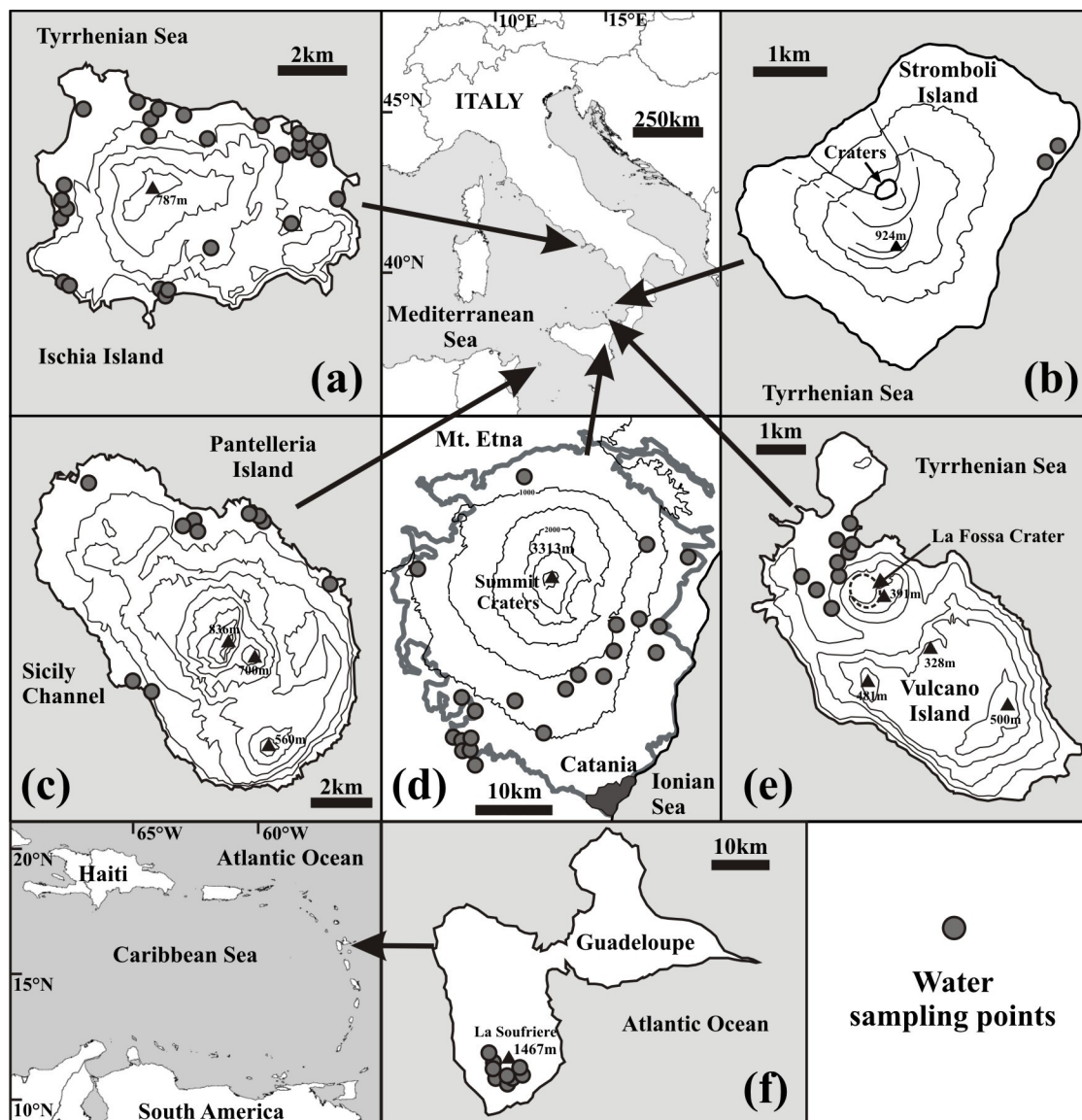


Figure 1- *Bagnato et al., 2008*

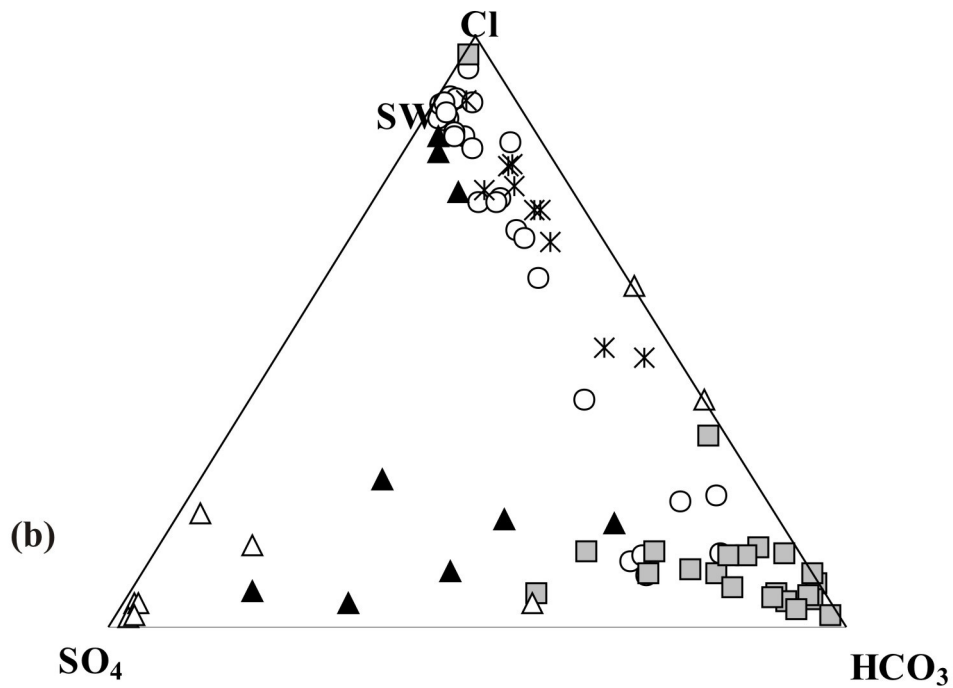
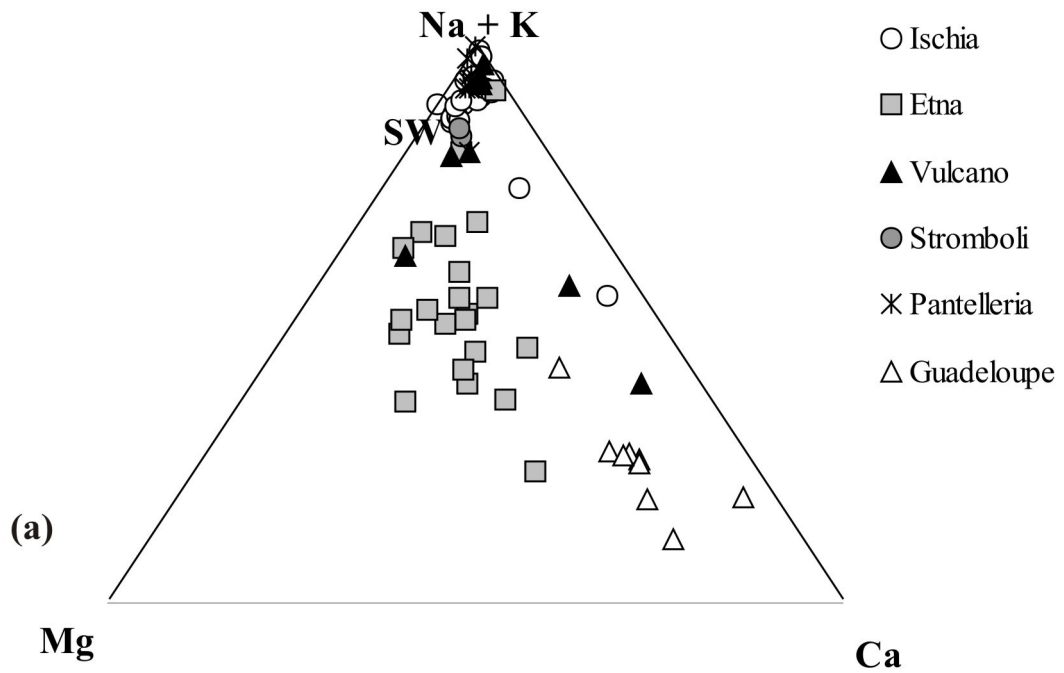


Figure 2- *Bagnato et al., 2008*

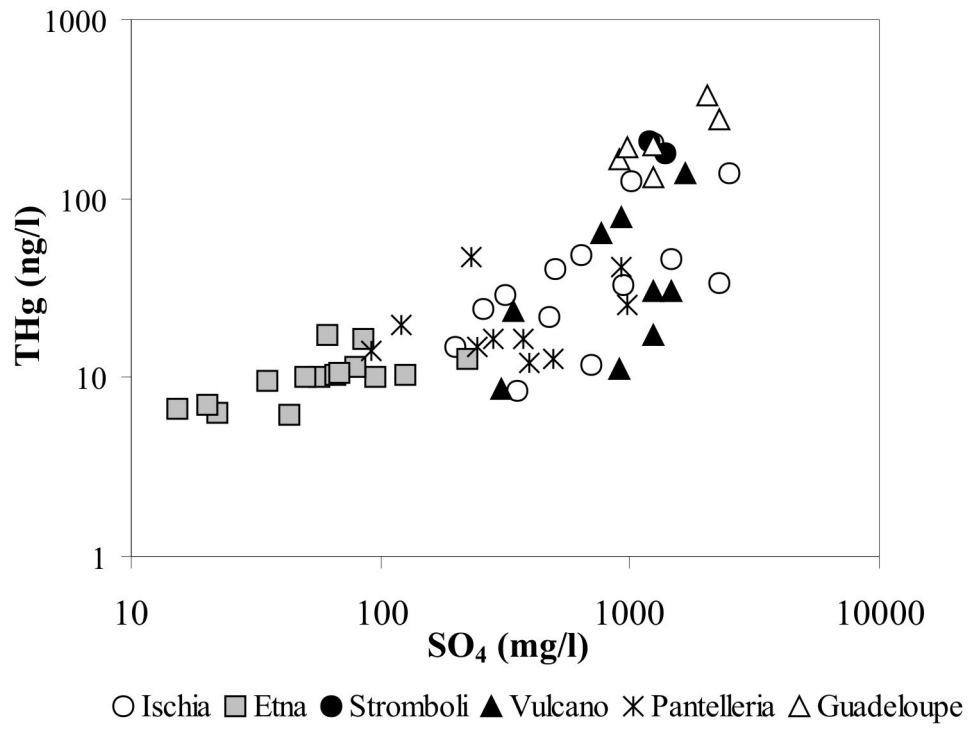


Figure 3- *Bagnato et al., 2008*

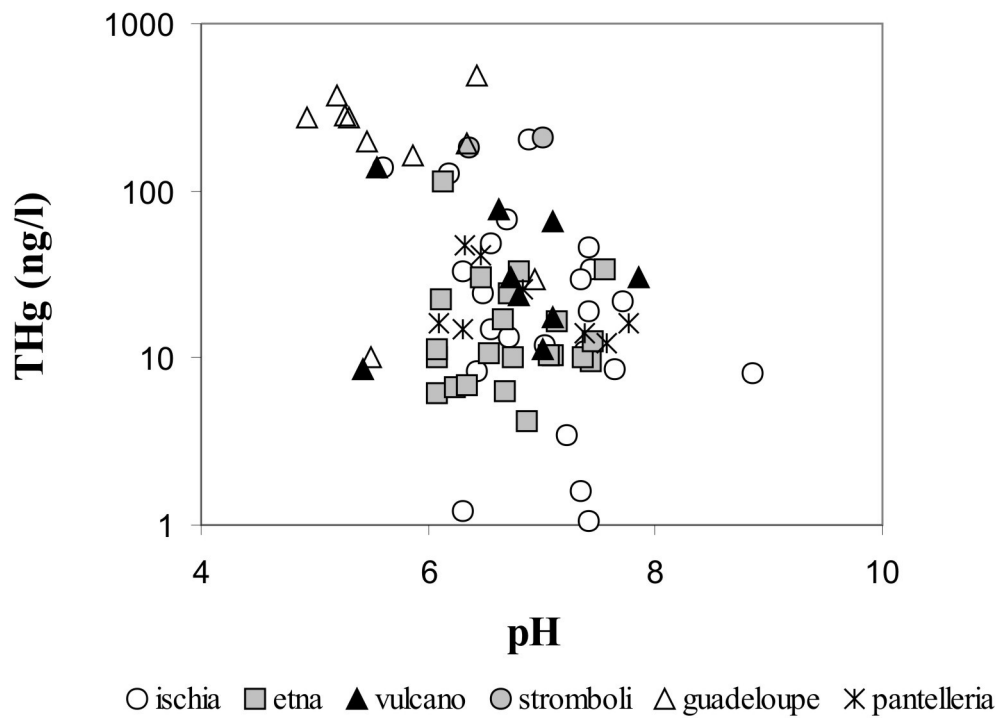
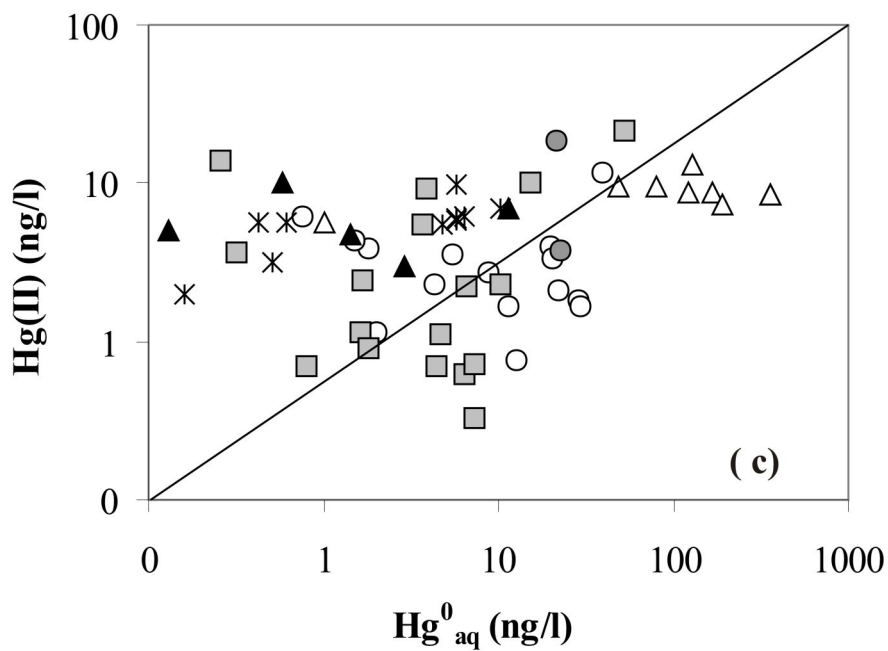
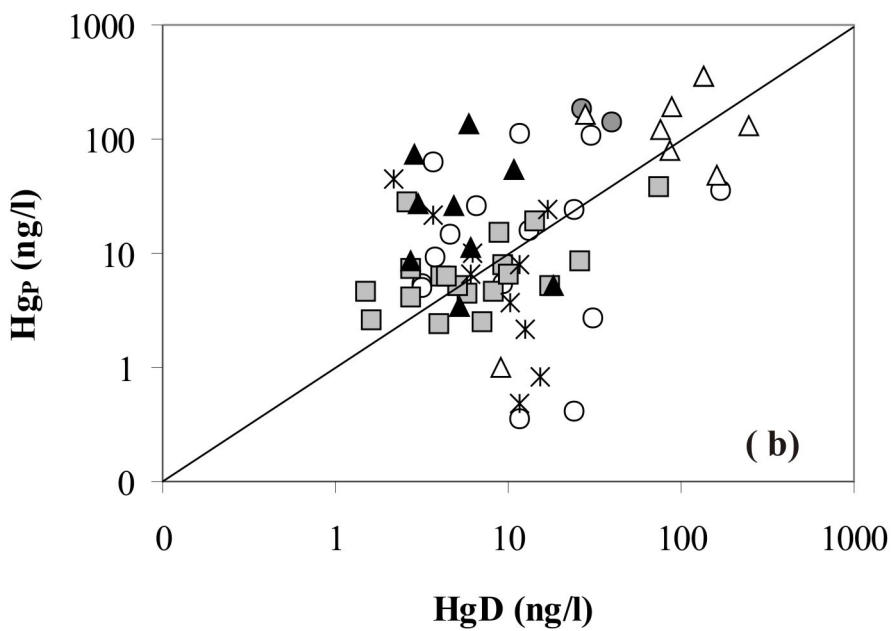
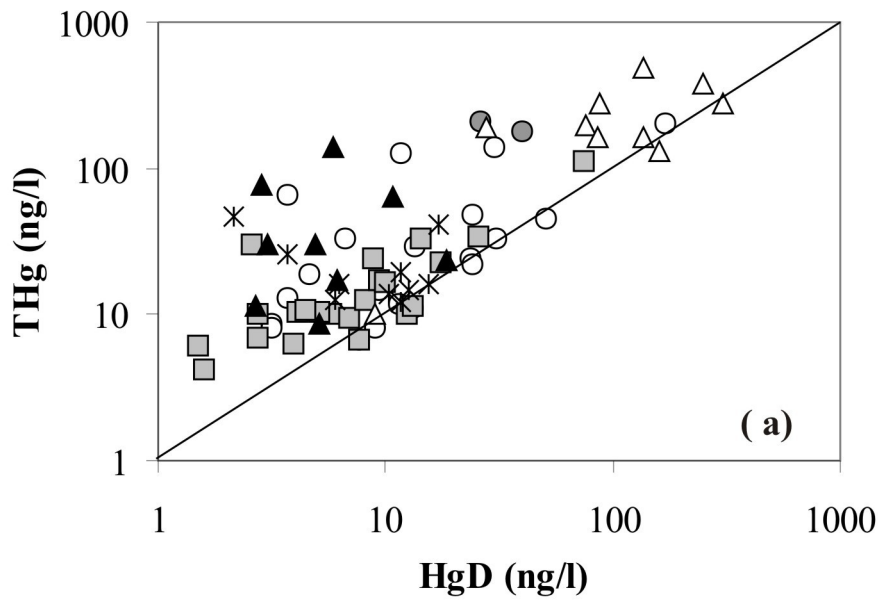


Figure 4- *Bagnato et al., 2008*

Figure5

[Click here to download Figure: Figure 5.pdf](#)



○ ischia □ etna ▲ vulcano ● stromboli ✖ pantelleria △ guadeloupe

Figure 5- Bagnato et al., 2008

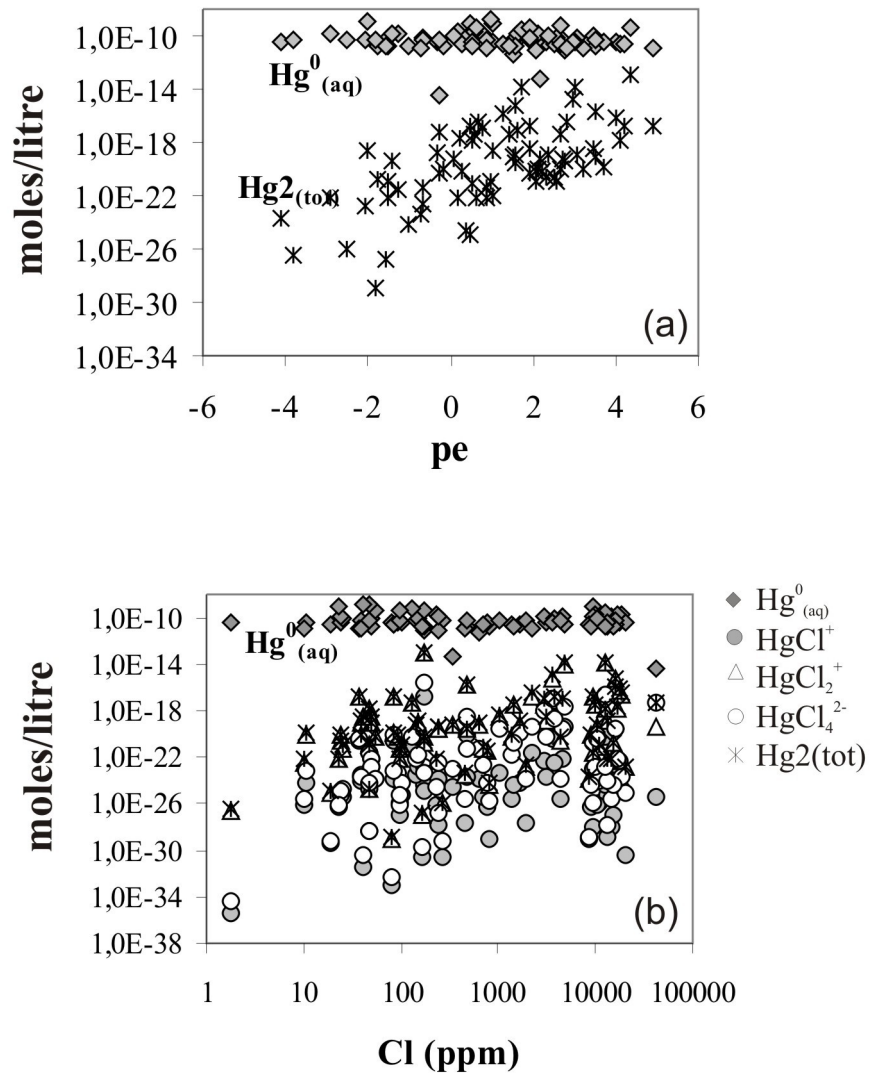


Figure 6- Bagnato et al., 2008

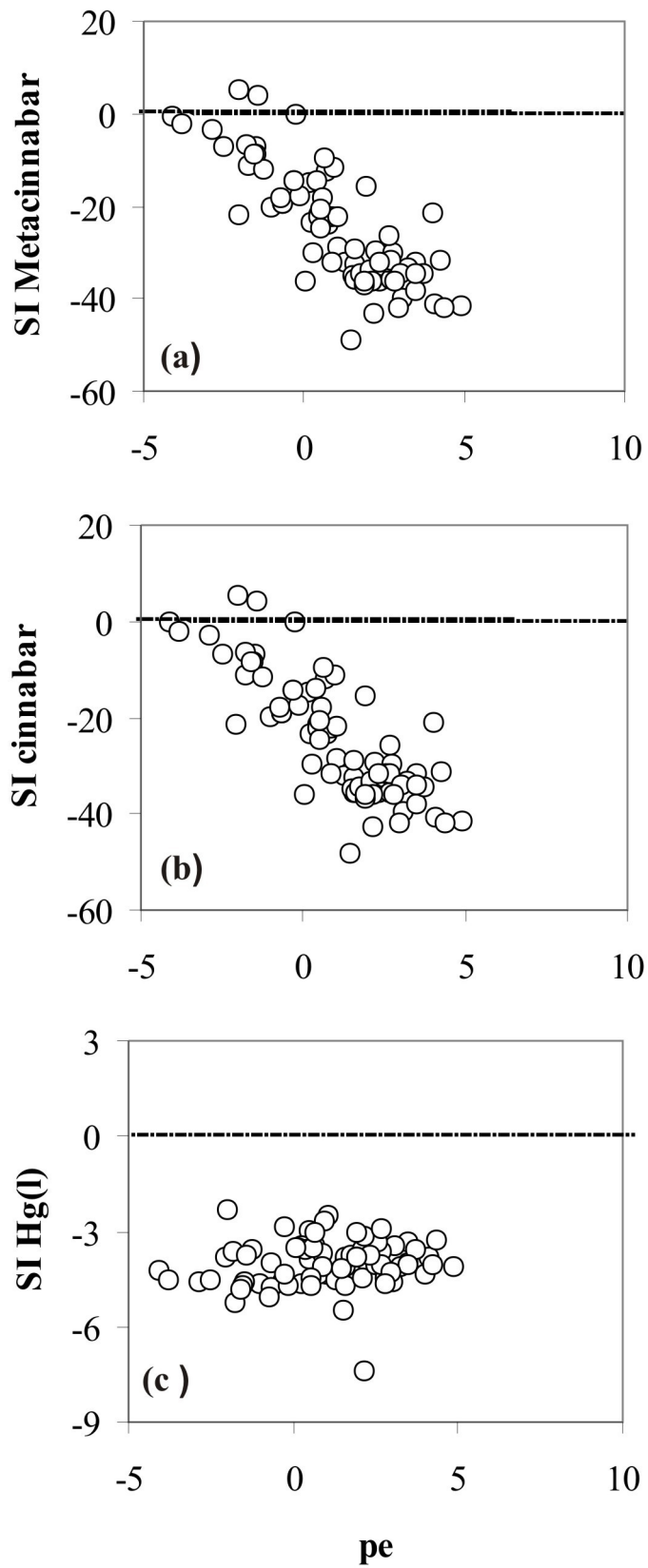


Figure 7- *Bagnato et al., 2008*

Figure8

[Click here to download Figure: Figure 8.pdf](#)

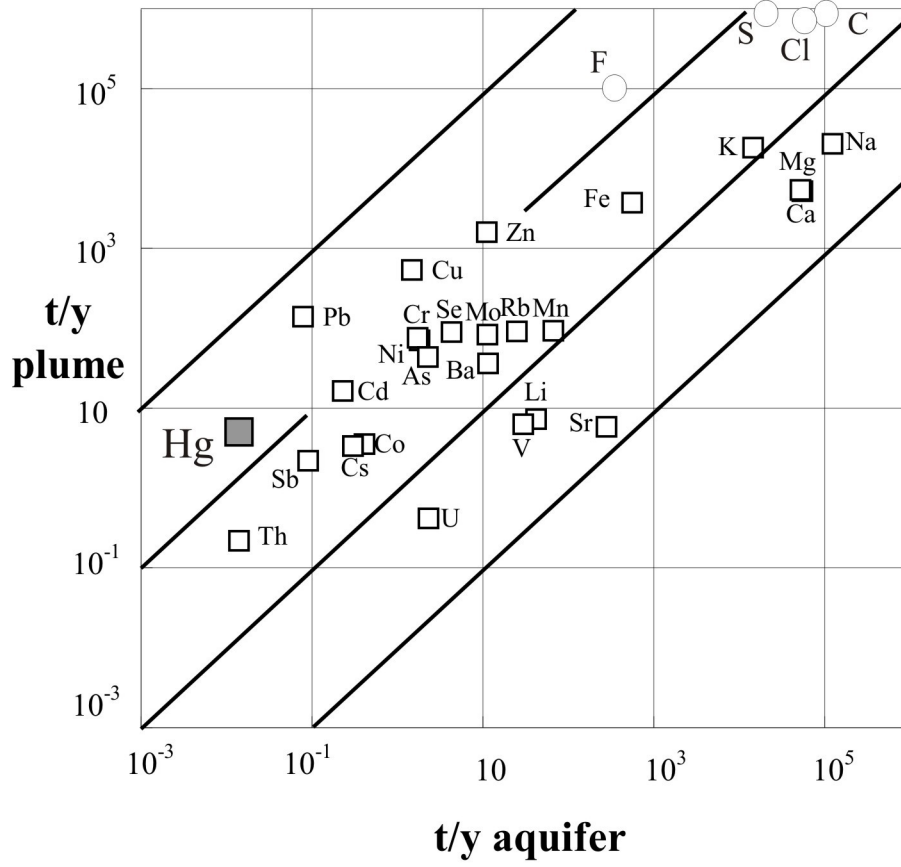


Figure 8- Bagnato et al., 2008

Table1

[Click here to download Table: Table 1.doc](#)

Table 1

Water Point	T(°C)	pH	Eh (V)	Na	K	Mg	Ca	HCO ₃	Cl	SO ₄	NO ₃	TDS	THg	HgD	Hg(II)	Hg _P	Hg ⁰ _{aq}
Mt. ETNA																	
Cherubino	13.9	6.74	0.233	104	21.5	94.0	40.1	738	47.5	56.6	17.4	1119	10.2	5.1	1.1	5.1	4.0
Acqua Bongiaro	14.7	7.10	0.027	31.0	8.21	29.9	38.7	177	18.8	125	1.24	429	10.4	5.1	0.7	5.2	4.4
Pedara	14.8	7.43	0.133	54.0	10.2	20.5	12.8	207	24.5	35.0	4.9	368	9.5	6.9	0.6	2.5	6.3
Romito	15.2	6.71	-0.103	149	19.5	115	48.5	1000	80.5	4.8	< 1	1417	24.2	8.7	2.2	15.4	6.5
Guardia	15.4	6.11	0.199	72.9	20.7	45.6	41.5	378	50.3	82.1	21.7	712	22.7	17.5	0.1	5.2	n.a.
Rocca Campana	13.0	7.36	0.175	86.2	14.1	36.1	14.2	293	38.6	95.5	0.6	578	10.2	12.5	2.3	n.a.	10.3
Ciapparazzo	11.6	7.45	0.120	156	19.9	77.6	23.1	451	99.6	222	3.7	1052	12.7	8.1	0.7	4.6	7.4
Ponteferro	15.4	6.07	0.280	84.1	18.0	82.0	76.5	759	37.2	49.9	8.7	1115	10.2	2.7	1.1	7.4	1.6
Avana	18.5	7.07	0.120	223	24.6	112	93.2	1037	172	66.2	37.2	1765	10.3	4.1	2.4	6.3	1.6
S26	19.6	6.87	0.145	241	46.5	109	89.4	881	169	255	5.6	1796	4.2	1.6	<0.5	2.6	1.6
Ospedale	16.5	6.68	0.201	125	19.5	88.0	87.6	955	48.9	22.1	7.4	1353	6.4	3.9	3.6	2.4	0.3
Ossidi	19.3	6.66	0.050	618	30.9	147	153	1555	773	61.0	11.8	3349	17.2	9.3	5.5	7.9	3.7
Gennaro	16.7	7.14	0.155	186	22.1	106	94.8	939	142	85.9	37.2	1613	16.5	9.9	<0.5	6.6	9.8
Costanzo	18.5	6.08	0.160	182	29.1	243	130	1662	239	43.2	10.5	2538	6.2	1.5	0.7	4.7	0.8
Ilice	10.2	6.24	0.210	30.3	8.21	14.8	17.2	180	10.6	15.4	2.5	278	6.7	7.7	<0.5	n.a.	7.4
Currone	15.2	6.34	0.185	105	18.8	71.4	51.9	698	39.7	20.2	8.7	1013	6.9	2.7	0.9	4.21	1.8
Fisauri	10.5	6.8	0.145	49.0	9.38	25.8	43.9	296	24.8	43.7	8.0	500	33.3	14.2	13.9	19.1	0.3
Acqua Grassa	19.3	6.07	0.022	171	18.0	140	124	1403	48.2	78.7	21.7	2004	11.4	13.1	9.2	n.a.	3.8
Torrerossa	13.2	7.56	0.122	167	10.2	25.8	16.8	244	24.5	29.3	8.0	525	34.3	25.6	10.2	8.68	15.4
S. Giacomo	12.1	6.46	0.049	26.2	8.21	44.4	67.9	494	10.3	6.24	< 1	657	30.3	n.a.	6.5	27.7	n.a.
Piano Elisi	20.4	6.53	0.156	97.7	25.8	71.1	40.7	537	84.0	68.6	< 1	924	10.7	n.a.	8.2	6.28	n.a.
Salinelle Stadio	28.0	6.13	-0.020	24074	557	345	1814	171	41178	1233	14.4	69386	113	74.8	21.7	37.8	53.1
STROMBOLI ISLAND																	
Fulco	41.8	6.36	0.037	5352	360	703	425	653	9881	1396	8.0	18778	181	40.1	18.4	141	21.6
Zurro	35.9	7.00	-0.077	5224	269	632	338	253	9546	1198	19.8	17479	208	26.3	3,8	182	22.5
VULCANO ISLAND																	
Bambara	22.6	5.43	0.248	71.5	30.4	20.4	137	653	82.9	1396	8.0	2399	8.6	5.2	5.0	3.4	<0.5
Bartolo	79.5	7.10	-0.047	490	226	5.76	20.6	253	96.2	1198	19.8	2309	64.8	10.7	10.1	54.1	0.6
Camping Sicilia	51.2	7.85	0.020	1241	268	47.8	70.8	201	1404	303	42.2	3577	30.5	4.9	6.0	25.7	n.a.
Casamento	34.5	6.80	0.140	185	49.5	36.5	142	650	149	768	6.2	1986	23.7	18.5	7.0	5.3	11.5

Castello	34.5	5.54	-0.250	4471	135	592	498	345	8714	1467	3.1	16225	139.2	5.8	3.0	133.4	2.9
Discarica	47.6	6.63	-0.100	469	237	322	106	406	166	340	172	2218	77.7	n.a.	4.9	74.8	n.a.
EAS	46.0	6.72	-0.010	4576	224	795	395	515	8807	1676	< 1	16988	30.2	3.0	4.9	27.2	n.a.
Lentia	48.4	7.10	0.033	1006	214	29.2	52.0	2430	708	924	< 1	5363	17.3	6.1	4.7	11.2	1.4
Muscarà	61.2	7.00	-0.049	540	150	37.1	111	442	450	906	< 1	2636	11.3	2.7	4.8	8.6	n.a.
PANTELLERIA ISLAND																	
Cala Tramontana	29.6	7.77	0.116	796	39.1	34.6	22.9	427	1022	120	29.8	2491	19.5	11.6	5.8	7.9	5.8
Armani	23.1	9.66	0.085	1308	21.1	0.49	3.81	284	1476	246	< 1	3339	14.7	12.6	6.2	2.1	6.4
Gadir	53.8	6.33	0.196	3326	164	181	114	1141	4795	496	< 1	10217	12.6	6.0	5.6	6.6	0.4
Buvira Gadir	33.6	7.58	0.116	2701	140	122	90.4	1189	3707	374	18.6	8342	16.3	15.5	9.3	0.8	6.2
Daietti	36.4	6.10	0.215	398	30.5	55.5	46.1	433	470	92.2	121	1646	14.0	10.3	5.5	3.7	4.8
Scauri	38.2	7.37	0.183	2489	144	87.6	60.1	723	3629	285	34.1	7451	16.3	6.2	5.6	10.1	0.6
Polla 3	55.0	6.30	-0.019	3198	156	131	110	1467	4391	393	< 1	9846	12.1	11.6	5.9	0.5	5.7
Buvira Rizzo	34.3	6.83	0.171	2168	106	131	60.3	2422	2197	231	< 1	7315	47.3	2.2	2.0	45.2	<0.5
Lago	25.2	9.11	0.004	7916	344	198	3.21	2047	10293	918	< 1	21719	41.2	17.0	6.8	24.2	10.2
La Vela	50.1	6.47	0.034	7643	406	367	215	589	12342	968	< 1	22530	25.6	3.71	3.2	21.9	0.5
ISCHIA ISLAND																	
La Pergola 2	42.6	7.64	-0.060	979	79.8	30.4	46.7	973	823	354	75.6	3361	8.5	3.2	3.6	5.33	n.a.
S. Michele	46.1	6.89	0.030	5710	164	451	247	335	9556	1235	< 1	17698	205	169	n.a.	36.1	n.a.
Safen Citara	91.0	6.55	-0.209	8634	608	273	380	226	14332	633	< 1	25086	48.6	24.0	2.11	24.6	21.9
Nitrodi	28.0	6.56	0.132	179	23.5	17.2	149	543	91.5	198	65	1266	14.8	9.3	0	5.5	9.3
Giardino delle Ninfe	34.4	5.60	0.042	10282	442	1293	453	589	18970	2513	< 1	34542	138	30.2	1.8	108	28.3
Thermal C. 1	46.6	6.30	-0.060	10321	495	1144	524	1467	17554	2187	< 1	33692	n.a.	6.9	6.2	n.a.	0.7
Thermal C. 2	47.9	7.22	0.065	2101	142	97.9	110	717	3059	444	26.7	6697	3.5	5.6	3.8	n.a.	1.8
Cristallo	28.1	7.84	0.094	1314	65.7	61.2	82.4	808	1660	347	100	4438	n.a.	5.8	4.3	n.a.	1.5
Elisabetta	54.0	7.68	0.140	1128	97.0	0.51	12.0	1870	343	610	4.34	4064	<0.5	<0.5	1.4	n.a.	n.a.
Ambasciatori	26.7	8.85	-0.122	11572	455	1417	8.62	372	20696	2082	71.3	36673	8.1	9.0	3.6	n.a.	5.4
Grazia Terme	67.0	7.03	-0.170	1211	100	4.37	23.2	2108	273	697	< 1	4416	11.9	11.5	2.7	0.3	8.8
Hotel Tritone	33.9	7.43	0.015	9427	439	1061	368	528	16644	2268	13.0	30748	33.6	30.8	1.6	2.7	29.2
Galidon	74.0	6.48	0.053	3047	126	31.5	188	772	4637	256	< 1	9057	24.2	23.8	4.0	0.4	19.8
S. Leonard	47.0	7.42	0.081	9250	353	1098	359	311	15845	2279	< 1	29495	19.2	4.6	7.5	14.6	n.a.
S. Leonard 2	36.6	7.38	0.098	9416	371	1120	370	326	16091	2325	< 1	30019	11.0	13.0	1.6	n.a.	11.4

Felix	39.0	7.35	-0.043	1388	111	60.7	58.7	619	1902	315	51.5	4505	29.3	13.3	0.7	16.0	12.5
Oriente	42.8	6.42	-0.095	7827	410	838	385	1464	13129	1669	< 1	25722	8.2	3.1	1.2	5.1	1.9
Edera	52.6	6.26	-0.099	11313	694	1242	645	1266	20315	2739	< 1	38214	n.a.	10.8	14.2	n.a.	n.a.
Fiola	56.0	7.42	0.099	1207	156	4.37	24.5	2019	636	361	14.3	4422	1.1	0.9	1.6	0.2	n.a.
Continental Mare	33.9	7.58	0.103	1682	106	57.7	52.1	790	2224	365	80.6	5357	<0.5	<0.5	1.4	n.a.	n.a.
Continental	44.0	7.71	0.101	1900	228	112	128	701	2979	478	40.3	6566	21.9	23.9	3.4	n.a.	20.5
Villa Bianca	91.0	6.19	-0.110	6774	274	254	253	290	10799	1003	< 1	19647	125	11.6	n.a.	114	11.6
Emanuela	83.8	6.71	-0.124	8573	381	830	295	171	15424	1878	< 1	27552	13.1	3.7	14.0	9.4	n.a.
Aphrodite	60.1	7.41	0.115	7470	314	596	277	168	12822	1474	44.6	23165	46.0	50.7	11.7	n.a.	38.9
Villa Svizzera	56.7	6.30	-0.020	8347	477	251	512	769	13324	935	< 1	24615	32.8	6.6	2.3	26.1	4.3
Hotel Principe	47.0	6.69	0.100	827	77.4	22.6	63.3	1546	479	144	64.5	3223	66.8	3.7	n.a.	63.1	3.7
GADELOUPE ISLAND																	
Bains Jaunes	29.8	5.26	0.116	37.1	5.69	24.7	98.1	18.3	55.4	1246	0.7	1485	279	230	9.5	49	220
Beausoleil	21.8	6.93	0.061	23.2	5.92	17.0	62.7	25.0	23.1	1248	4.4	1409	193	28.0	8.7	165	19.3
Chutes du Carbet	45.0	6.34	0.275	81.5	20.0	41.9	96.6	153	171	906	1.6	1471	277	304	7.4	n.a.	296
Gallion	44.2	4.93	-0.091	57.9	17.3	69.8	258	36.0	240	981	1.6	1661	10.0	9.0	5.7	1.0	4.2
Matouba	58.5	5.50	-0.250	56.3	9.27	14.5	268	23.8	1.77	17.4	4.3	395	164	85.2	9.5	79.1	75.7
Tarade	36.8	5.87	0.164	81.5	16.2	64.9	196	94.6	129	682	2.3	1266	277	87.3	7.4	190	80.0
Rav Marc	43.5	5.30	0.060	43.9	15.9	36.0	143	78.1	48.6	533	1.3	899	198	76.0	8.7	122	67.3
Pas de Roy	33.5	5.46	0.039	50.0	9.25	38.0	128	52.5	96.9	2292	16.8	2683	376	247	13.1	129	234
Carbet l'Echelle	21.2	5.19	-0.118	28.7	6.10	53.8	220	55.5	39.9	2047	4.4	2455	279	230	9.5	49.0	220
La Vela	50.1	6.47	0.034	7643	406	367	215	589	12342	968	< 1	22530	25.6	3.71	3.2	21.9	0.5
Mediterranean Seawater	20.0	8.20		11890	412	1422	359	165	21640	2994		38882	0.30*				

The prevailing excess of HgD with respect to THg exhibited by few samples could be due both to the analytical error estimated at about $\pm 10\%$ and contamination during the adopted sampling procedure.

* Mean value taken from Horvat *et al.*, 2003

n.a.: not analysed sample.

Table 2

Cinnabar	$\text{HgS}_{(s)} + \text{H}^+_{(aq)} = \text{Hg}^{++}_{(aq)} + \text{HS}^-_{(aq)}$	$\log K_{(25^\circ\text{C})} = -40.228^{(a)}$
Metacinnabar	$\text{HgS}_{(s)} + \text{H}^+_{(aq)} = \text{Hg}^{++}_{(aq)} + \text{HS}^-_{(aq)}$	$\log K_{(25^\circ\text{C})} = -39.835^{(a)}$
Elemental mercury $\text{Hg}^0_{(l)}$	$\text{Hg}^{++}_{(aq)} + 2\text{e}^-_{(aq)} = \text{Hg}^0_{(l)}$	$\log K_{(25^\circ\text{C})} = -28.8^{(b)}$

(a) values calculated by HSC model.

(b) value by Stumm & Morgan (1996).