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Istituto Nazionale di
Geofisica e Vulcanologia

Segreteria di Redazione
Francesca Di Stefano - Referente
Rossella Celi
Tel. +39 06 51860068
redazionecen@ingv.it

in collaborazione con:
Barbara Angioni (RM1)

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CONTINUOUS GAS SAMPLING AND ANALYSIS AT THE PISCIARELLI FUMAROLIC FIELD (CAMPI FLEGREI) BY USING A QUADRUPOLE MASS SPECTROMETER (QMS)

Alessandro Fedele[1], Maria Pedone[1], Roberto Moretti[2], Renato Somma[1], Thomas Wiersberg[3],
Claudia Troise[1] and Giuseppe De Natale[1]

[1]**INGV** (Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Napoli - Osservatorio Vesuviano)
[2]**SECONDA UNIVERSITÀ DI NAPOLI** (Dipartimento di Ingegneria Civile, Design, Edilizia e Ambiente, Aversa - CE)
[3]**GFZ** (Deutsches GeoForschungsZentrum, Helmholtz-Zentrum, Potsdam)

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Introduction

Volcanic monitoring has as main goal the identification of typical phenomena of impending-eruption precursors. Therefore, recording a large amount of data of volcanic gases composition, during the quiescence period, is fundamental in order to identify baseline values to be distinguished from any anomalous geochemical signal. The gases emitted by most of the volcanoes are difficult to be sampled especially when the volcano is restless. Volcanic gases have traditionally been monitored by means of direct in situ sampling of fumaroles, followed by laboratory analysis [e.g., Symonds et al., 1994]. However, since direct sampling is often impractical and hazardous, particularly during eruptions, or of too low temporal resolution, efforts have been made (since the 1970s) to improve volcanological applications of optical remote sensing techniques [Pedone et al., 2014; and references therein]. Soil-gas surveys of hydrothermal volcanoes in a quiescent condition have also quantified diffuse CO_2 emissions, but much less information has been obtained on fumarolic CO_2 emissions. Because of these difficulties, the volcanic CO_2 flux (the most reliable gas precursor to an eruption, [Aiuppa et al., 2015]) inventory remains sparse and incomplete for most of the active volcanoes on Earth [Burton et al., 2013]. Collection of fumarole gases is – depending on the state of volcanic activity, for logistics and other practical reasons – mostly performed discontinuously with time intervals ranging from days, weeks or even months between consecutive sample collections [Pecoraino and Giammanco, 2005]. Conventional sampling requires that operators collect fluid samples directly from the fumarolic vent in different kind of flasks directly on site. By this way any short-term variation in gas-geochemical parameters may be missed.

These sampling frequencies could be too low to allow for an efficient comparison between gas data and continuous geodetic, seismic of geophysical monitoring information, and have to be calibrated in function of the geochemical tracer to investigate, and thus of the sector of volcano plumbing system. In addition, scientists are at serious risk of being directly exposed to potential hot and toxic gases while gathering samples, but in the last decades automatic systems have been developed (MultiGAS, [Aiuppa et al., 2007; Aiuppa et al., 2013; Shinohara, 2005]) and several new techniques are in experimental phase (TDL, [Pedone at al., 2014; DIAL, Aiuppa et al., 2015]) to become a "springboard" in geochemical monitoring. Few application of continuous gas-monitoring system based on quadrupole mass spectrometer have been discussed in literature. Continuous measurement of dissolved gas concentrations using a quadrupole mass spectrometer was described by Takahata et al. [1997]. A system which analysed fumarolic gases pumped through a pipe to a station composed of a gas chromatograph, a mass spectrometer and several other physical instruments was described also by Faber et al. [1998]. Other techniques for continuous gas monitoring have been applied on several volcanoes. Toutain et al. [1992] present data from a system to monitor CO_2, He and 222Rn in gases from a well located at the base of the active cone on Vulcano Island, Italy. Shimoike and Notsu [2000] report on a system to monitor volcanic gases extracted from an observation well located 3 km north of the summit of the Izu-Oshima Volcano, Japan.

Nevertheless only limited technical information is available on systems of equipment for continuous monitoring which can be directly connected to active fumaroles. Zimmer and Erzinger [1998] and Zimmer et al. [2000] present data from a gas chromatograph based system operating continuously at the summit of Merapi Volcano. Faber et al. [1998] showed a system which analyzed fumarolic gases pumped through a pipe to a remote station where several instruments (e.g. gas chromatograph and mass spectrometer) monitored various physical and chemical parameters.

Most of volcanic monitoring at Pisciarelli, located immediately on the eastern side of Solfatara crater, in correspondence of a seismogenetic fault, is carried out discontinuously. In particular discontinuous gas analysis at Pisciarelli started in 1999 [Chiodini et al., 2000] and the geochemical monitoring with a sampling frequency of less than one per month is still done from Osservatorio Vesuviano (INGV of Naples). The flux of carbon dioxide dissipated in diffuse form via the soil has been characterized since Chiodini et al. [2001]. In contrast, the gas output sustained by fumarolic activity was unconstrained (before the campaigns carried out from Aiuppa et al. [2013] and Pedone et al. [2014]), which reflects current technical inability to make gas flux estimates at low-temperature fumarolic fields, where sulphur dioxide (SO_2) is typically absent, and conventional ultraviolet sensing techniques (e.g., Oppenheimer, 2010) are therefore useless [Aiuppa et al., 2013].

To fill this gap in knowledge is now more important than ever, considering the visible (not always quantified) increase in flow rates at the fumaroles, including small events of dark mud expulsion at Pisciarelli [Chiodini et al., 2010; 2011; Aiuppa et al., 2013]. Continuous gas monitoring at Pisciarelli was applied using an automatic station (FLXOV3) to measure soil CO_2 fluxes, installed for the first time in

March 2002, but it was seriously damaged many times during the period 2002–2005; therefore, the data set for this period is largely incomplete [Chiodini et al., 2010]. Therefore there are not applications about innovative system consisting in sampling gas directly from the main fumaroles in Campi Flegrei caldera by using QMS. In recent time, changes occurred in this geothermal field show an evident increase of the activity compared to previous inspections [Chiodini et al., 2010; 2011; Aiuppa et al., 2013]; a resumption of ground uplift since 2005 [Troise et al., 2007] and a progressing increase in the CO_2-rich magmatic contribution to fumarolic fluids since 2000 [Chiodini et al., 2012].

Starting from 2003 the area was affected by an increase in discharge temperature of the fumaroles (from 90 to > 100 °C) highlighting a strong increase in fumarolic flow rate from 2005 to 2013 [Chiodini et al., 2015], local seismic activity [D'Auria et al., 2011] and by some macroscopic changes such as the appearance of a vigorous degassing vent (March 2009) currently the main active gas source at this site (T ~ 110 °C), a mud bubbling pool (T ~ 90 °C) which was probably accompanied by a small explosion [Chiodini et al., 2011] and a small active fumarolic field in the southern part of the area.

Consequently, at the beginning of 2009, a continuous gas monitoring station, mainly equipped with a quadrupole mass spectrometer (QMS Pfeiffer Omnistar©), was installed at Pisciarelli site.

Several chemical species concentrations are detected in the fumarolic emission with an high sampling rate (very short intervals of measurements down to 1 second) as well as the fumaroles' temperature. Although numerous technical problems were addressed due to the ephemeral emission point, coupled with the harsh environment, a good statistic record and a reconstruction of the gases evolution of the investigated area was obtained. Fluctuations in the gas composition and variations in the monitored parameters which show the main relationships of good tracer of magmatic fluids injection such us CH_4/CO_2 and He/CH_4 are also reported.

The overall purpose of our research is to explain technical information on continuous monitoring gases emitted from the main fumaroles and to detect the effects of changes in gas components ratios at depth.

1. Geological background of Campi Flegrei

Located in the Campanian region (Southern Italy), the Phlegraean Volcanic District (PVD) is a densely populated active volcanic area, including the Campi Flegrei caldera (CFc), the islands of Procida and Ischia, plus a number of submerged volcanoes. Volcanological, geophysical and geochemical evidences [de Vita et al., 1998; 1999] support the hypothesis that remnants of the magma source feeding the two large eruptive events of Campanian Ignimbrite (37 ky BP) and Neapolitan Yellow Tuff (14.9 ky BP) are involved in more recent volcanic episodes (e.g. Agnano-Monte Spina eruption, 4 ky BP). Volcanic risk has increased through time as a consequence of rapid population expansion in such active and potentially active volcanic areas of the Earth. Therefore the restless Campi Flegrei caldera (CFc) is one of the most dangerous volcanic areas on Earth, which has recently shown some of the most unambiguous signs of potential reawakening [Aiuppa et al., 2013], with phases of up-lift and subsidence over a range of timescales [Rosi et al., 1983; Di Vito et al., 1999; Orsi et al., 2004; Morhange et al., 2006], and evidence of decades-long inflation prior to the last magmatic eruption [Dvorak and Mastrolorenzo, 1991]. It is inhabited by more than 1.5 million people, most of whom live in the city of Naples.

The Monte Nuovo eruption was followed by a long period of subsidence, culminating in two major uplift and seismic episodes ('bradyseisms'), which occurred in 1969–1972 and in 1982–1984, which have shown a total vertical displacement of 3.8 ± 0.2m [Del Gaudio et al., 2010, and references cited therein]. In 1982–1984, the maximum uplift of 1.8 m was accompanied by ~16,000 shallow earthquakes that affected CFc, which caused the partial evacuation of the heavily populated town of Pozzuoli [Barberi et al., 1984].

Since 1985, CFc has been slowly subsiding, which has been interrupted by a few minor uplift events. In 2005, there was new inflation, which accelerated and reached a maximum vertical displacement of about 23 cm by June 2014 [Chiodini et al., 2015]. This last stage was accompanied by weak seismicity, by a strong increase in fumarolic activity, and by important compositional variations in the fumarolic effluents, which were interpreted as increased contributions from a magmatic source [Chiodini et al., 2012, and references therein].

Presently, the area is affected by intense, diffuse degassing and fumarolic activity in the both Solfatara crater and Pisciarelli fault [Pedone et al., 2014]. Detailed geochemical analysis of the fumaroles [Caliro et al., 2007], coupled with the measurements of soil diffuse degassing [Chiodini et al., 2001; 2015] and with physical numerical simulations of the hydrothermal system [Todesco et al., 2003], suggests that magma degassing episodes have a relevant role in triggering the volcanic unrest periods that periodically affect the area [Chiodini et al., 2003; Bodnar et al., 2007; Moretti et al., 2013] corroborating the role of fluids as drivers of periods of unrest at Campi Flegrei strongly supported by temporal coherence between changes in gas composition and uplift [Chiodini et al., 2010; Aiuppa et al., 2013].

2. The Pisciarelli site and its fumarolic activity

Pisciarelli area is a fault-related fumarolic field located at the south-eastern outer flank of the Solfatara crater (Fig. 1). This area is characterized by the presence of fractures and is affected by a consistent soil degassing and fluids emissions (Fig. 2). Chiodini et al. [2001] first identified a large diffuse degassing structure (DDS) with an anomalously high CO_2 flux release (locally up to 50,000 $g/m^2 \cdot d$) that included the Solfatara crater, a tuff cone near Pozzuoli that formed ~3.9 ka BP [Di Vito et al., 1999], and the Pisciarelli area, few hundred meters east of Solfatara. The fumaroles are mainly composed by H_2O followed by CO_2 and H_2S having surface temperatures between 100-110 °C [Chiodini, 2009]. Starting from 2003, the Pisciarelli field has experienced an evident increase of activity, which has been marked by a sequence of temperature peaks of the fumaroles above the average background temperature of 95 °C, each lasting up to half a year until early 2011, and exceptionally about one year, from mid-2011 to mid-2012, the last recorded peak [Chiodini et al., 2015]. Furthermore, a nearly linear trend of the peak temperatures, from about 97 °C up to around 112 °C, has been recorded from 2003 up to date [Chiodini et al., 2015]. Changes in intensity of fluids emissions were observed and an increase of soil CO_2 flux (FLXOV3) is shown (see bulletin of surveillance 2016, INGV-OV). Fracture is mostly trending the N110°/N290° direction and the area between Solfatara and Pisciarelli is dominated by an early regional NE-SW normal fault. This fault is the site of the well known fumaroles and mud pools of Pisciarelli [Isaia et al., 2015]. Also accumulations of material from surface gravitational movements of recent formation were observed.

Figure 1. The Campi Flegrei caldera and the Pisciarelli fumarolic field location.

Figure 2. Pisciarelli fumarolic field. In the foreground the main fumarolic vent and the bubbling mud pool are shown.

The emission of gases and fluids are affected by near-surface secondary processes of seasonal character that seem to mask the deeper signals related to the temperature-pressure changes occurring in the hydrothermal system [Chiodini et al., 2011], clearly observed, instead, inside the Solfatara crater at the Bocca Grande (BG) and Bocca Nuova (BN) fumarolic vents [Chiodini et al., 2011]. In January 2013 the appearance of a vent emitting high-pressure steam and liquid water up to 3-4 meters high were observed.

The observed phenomenon might be at least partly linked with heavy rainfall during the last week of January (INGV - Osservatorio Vesuviano bulletin of surveillance 02-02-2013).

Other authors [Aiuppa et al., 2013] reported an increase of fumarolic CO_2 output in the campaign carried out at the end of January 2013 and an unusually strong >3 m high jets of gas and hot water occurred during the survey.

3. Gas Mass Spectrometry

3.1 Sectorfield vs. Quadrupole Mass Spectrometry

For determination of stable and noble gas isotopes, sector field mass spectrometers are commonly used. These instruments allow determination of isotopes with high resolution and with acceptable sensitivity. High resolution is needed to separate e.g. $^3He^+$ (m/u = 3.016) from HD^+ (m/u = 3.022) and H_3^+ (3.024), A = m/Δm ~500, which requires large magnetic fields and long measurement times.

The measurements are commonly done in a static mode, i.e. the mass spectrometer is not pumped during the measurement. This causes an increase of background signals during the measurement from leaking and memory effects. During the measurement, only a limited mass range can be passed through. Therefore, all noble gases (He, Ne, Ar, Kr, Xe) are measured separately for noble gas isotope studies. The determination of isotopes of one noble gas takes 10-30 minutes. After the measurement, the recipient needs to be pumped again before the next gas species can be measured, resulting in measurement times for all noble gas isotopes in one single sample of half a day.

In contrast to sectorfield mass spectrometers, the quadrupole analyser can be used in dymanic mode, i.e. the gas is permanently introduced in the mass spectrometer and pumped from the recipient. The whole mass range can be passed through much faster, resulting in measurement times of less than one minute for a whole range of species (H_2, H_2S, He, Ar, CH_4, CO_2, N_2, O_2) with detection limits of <0.2 parts per million by volume (ppmv) for He, <1 ppmv for H_2, CH_4, and Ar, as well as <10 ppmv for O_2, N_2, and CO_2. Isobaric interferences with oxygen on the diagnostic mass over charge ratios [m/u]=32, 33 and 34 increase the detection limit for H_2S to 200 ppmv. However, resolution (0.5 u) and sensitivities (>0.1 ppmv) are much smaller than for sectorfield mass spectrometers.

The QMS used in this study is much smaller (40 kg total weight) than common sectorfield mass spectrometers. The quadrupole analyser consists of a 6 mm diameter rod system and a length of 100 mm. It allows detection of ions in the mass range of 0-100 u and is equipped with a Faraday cup and a Channeltron. The gas enters the quadrupole field at a pressure of ~4 x 10^{-6} mbar. The pressure is reduced from atmospheric (inlet pressure) through a capillary to 1-2 mbar and then further reduced through sequentially pumping to the 10^{-6} mbar range.

3.2 QMS operation

Before gases can be analyzed in the mass filter, they must first be ionized in an ion source by means of so-called electron bombardment. For this, neutral gas molecules are ionized by collision with electrons which are emitted from an electrically heated cathode (filament) and accelerated to an anode. The yield in ions depends on the electron energy and reaches a maximum at 50 to 150 eV acceleration voltages between cathode and anode, depending upon the type of gas. Single and multiple positive ions can be formed, depending on the ionization energy of the molecule and the energy of the colliding electron.

In our study, the acceleration voltage was set to 90 eV in order to achieve an acceptable ion yield at a relatively low yield of multiple charged ions. Multiple charged ions my cause significant isobaric interferences on mass-over-charge rations m/u=20 (^{20}Ne and ^{40}Ar^{2+}), m/u=22 (^{22}Ne and CO_2^{2+}). The resolution of the QMS does not allow discriminating between ^{20}Ne and ^{40}Ar^{2} respectively ^{22}Ne and CO_2^{2+}; we therefore do not report neon concentrations here.

Another phenomenon that may occur for ionized molecules is fragmentation, i.e. the decay of molecules into charged and neutrals fragments. This is relevant for CO_2^+ that may become fragmented into CO^+ and O: at the given acceleration voltage, about 10% of the ionized CO_2 decays into CO^+ (m/u = [28]) and O. However, m/u = [28] is also the relevant mass-over-charge ratio for nitrogen (N_2). The ratio CO_2^+/CO^+ was determined by regular calibration measurements of pure CO_2. N_2 on m/u=[28] was corrected by subtracting CO^+, which was calculated from the measured CO_2 concentration and the CO_2^+/CO^+ ratio determined before. Moreover, the N_2 concentration determined on m/u=[28] were compared with measurements of N_2 on m/u = [14] from N_2^{2+} and N^+ in order to avoid overestimation of N_2.

The amount of hydrocarbons is generally low in volcanic gases with methane concentration in the water-free gas phase of Pisciarelli volcanic gases in the range of 100 ppmv. Isotopic gas equilibria studies suggest that CH_4 is formed by reduction of CO_2 [Caliro et al., 2007] rather than by thermal degradation of organic matter. The amount of C^{2+} (ethane, propane...) in Pisciarelli volcanic gases can therefore be assumed being so low that formation of fragmented and/or multiple charged ions is negligible. Methane was determined on [m/u] = 15, with 85% yield, compared to [m/u] = 16 to circumvent the problem of isobaric interferences with O_2^{2+}.

After ionization, the gas is introduced in the quadrupole analyzer. The quadrupole analyzer is a device which uses the stability of the trajectories in oscillating electric fields to separate ions according to their m/u ratios. Quadrupole analyzers are made up of four rods of circular or, ideally, hyperbolic section. The rods must be perfectly parallel. The ions, accelerated by the plates accelerator, enter the tunnel bounded by the bars and are repelled by and attracted to the positive pole negative.

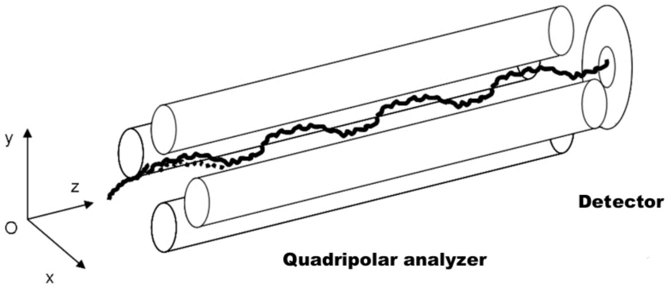

Figure 3. Sketch of a quadrupole analyzer.

However, due to the oscillation of the quadrupole ions assume a zigzag trajectory and ending with the discharge of one of the bars, except that, for a certain value of the oscillation frequency, have a kinetic energy such that the motion becomes sinusoidal and manage to get out of the tunnel and into the detection system (Faraday or Channeltron). The ions pass through the mass analyzer and, then, they are detected and transformed into a usable signal by a detector.

Detectors are able to generate from the incident ions an electric current that is proportional to their abundance. There are many types of detectors, but most work by producing an electronic signal when struck by an ion. Timing mechanisms which integrate those signals with the scanning voltages allow the instrument to report which m/z strikes the detector. The mass analyzer sorts the ions according to m/u and the detector records the abundance of each m/u. Regular calibration of the m/u scale is necessary to maintain accuracy in the instrument. Calibration is performed by introducing a well known compound into the instrument. The QMS used in the present study was equipped with two analyzers: a Faraday detector and a Channeltron. The Channeltron is about 100 times more sensitive than the Faraday. The Farady detector was used only for detection of CO_2 (<95 vol-%), all other gas species in our study were detected by the Channeltron.

After turning on the QMS it takes about 30 minutes to achieve the required vacuum in the recipient. However, several hours more are needed to achieve a stable electron emission from the filament and thus a stable signal. The QMS was controlled by the Quadstar software. The software was used to measure a set of gases (H_2, H_2S, He, Ar, CH_4, CO_2, N_2, O_2) minutely.

For quantitative analysis, the specific gas sensitivities were determined by calibration with air (for N_2, O_2 and He), pure CO_2, and a certified gas mixture for CH_4, H_2S, CO_2 and H_2 with the following composition: CH_4= 1009 ± 40 ppmv, H_2S= 1001 ± 40 ppmv, H_2= 987 ± 39 ppmv and CO_2= Rest. During air calibration, the capillary of the QMS was disconnected from the gas line and exposed to air. Air was used to calibrate for Oxygen, Nitrogen, and Helium. As internal standard, Ar was used.

During calibration with gas standards, the QMS was disconnected from the gas line and then connected to the calibration gas flask. After establishing the connection, the "dead volume" (i.e. the space between the inlet capillary of the QMS and the calibration flask) was evacuated by using the QMS for some time until a pressure inside the chamber of $<10^{-7}$ mbar was achieved. Then the calibration gas flask was opened to the QMS for measuring. Once calibrated, the QMS was ready to proceed with the quantitative analysis. Calibration measurements were performed weekly in order to minimize peak shifting.

4. Gas monitoring techniques

Mass spectrometry offers both multiple determination of chemical species, together with a large dynamic range of concentrations, from parts per billion (ppb) to percentage concentrations.

The equipment used consists of a quadrupole mass spectrometer (QMS) Omnistar® (Pfeiffer Vacuum, Germany) for the gas analysis, standard thermocouples, a field computer and a data logger for data storage. We used a small container to assemble the QMS close to the active fumarole (100 m) and we connected a continuous gas extraction device (100 m of Teflon tube 4mm internal diameter and 6mm external) directly into the vent.

Air conditioning was used to stabilize the temperature of the station and a UPS (Uninterruptible Power Supply) were used for data retrieval in case of power cut off. The water vapour in the gas was removed using two traps; the first one located 10 meters from the fumarole and a second placed inside the container before the QMS. The traps consist of a flagon placed inside a small field fridge at 4 °C and a peristaltic pump to remove the water condensed. The condensation issue can also be avoided by using a large degasser tank to collect gas from the bubbling pool and not pumping the gas, but let it free flow through the pipeline (as we did in the second phase in 2012). The gas was pumped by a membrane pump located in the monitoring station. The components of the gas monitoring system are shown schematically in figure 4.

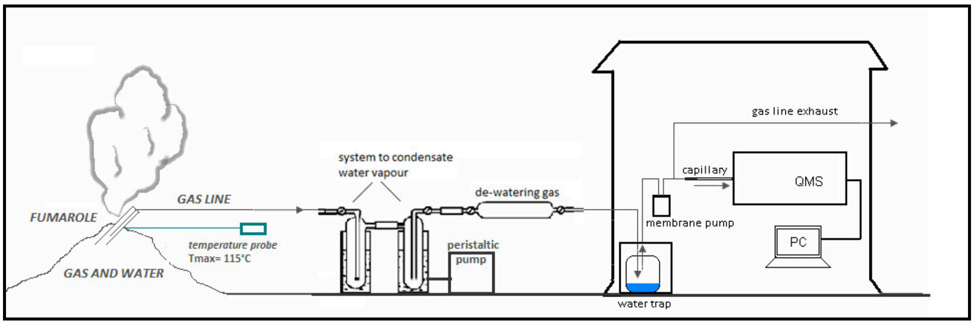

Figure 4. Gas monitoring system installed close to the fumarole. Fluids are driven by a membrane pump through a water trap in the QMS.

Because of the harsh environment, the system had to be changed and improved several times. The main difficulty was that the gas pipe connecting the equipment to the fumarole was often blocked by the condensation of the steam. The stability of the gas extraction device may be a problem due to ground landslides during the increase of the fumarole activity. Finally, there was a recurring power supply problem which can be damaged because of the high corrosive components in the volcanic fluids. It is for all those reasons that we recorded only limited data-set during which we have had the ideal condition to work.

5. Results

The first application for continuous sampling of fumarolic gases using a quadrupole mass spectrometer in the Pisciarelli began in January 2009. During this initial phase of sampling data were acquired continuously from 24th January until the April 2009. For some days the measurements were interrupted for re-calibration and maintenance of the instrument.

Several attempts have been tested to find an acceptable solution for an efficient removal of most of the water vapour or condensate and reproducible transfer of the gas components under investigation. In 2012 we tried again to obtain the continuous monitoring system and during twenty days among the months of May-June 2012 a new data-set was obtained.

Because the QMS has been set to acquire a measure per minute, an average of the values (about 1440 per day) was made. The large amount of data obtained allows us to observe short-term variations (daily/weekly variations) which often is not possible to observe by a discontinuous sampling.

In the following figures, the data-set averages obtained in 2009 and 2012 are plotted, compared with the data obtained by Caliro (pers. comm.) by INGV-laboratory measurements on gas samples collected discretely during the same period using Giggenbach method and chromatographic analysis. The first evidence that we can observe is the large amount of data collected automatically by our monitoring system.

The He/CO_2, H_2S/H_2 and CH_4/CO_2 ratios were used to detect magmatic/hydrothermal component in the system. In fact methane is a gas species which differentiates in hydrothermal systems, where it is present in relatively high concentrations, from high temperature volcanic/magmatic fluids where it is normally absent or present in very low concentrations [Chiodini, 2009; Chiodini, 2012]. At the beginning of our campaign (2009), the CH_4/CO_2 ratio values are in line with discrete sampling data (Caliro pers. comm., Fig. 5); unfortunately, this does not occur with the progress of 2009 campaign, as our trend reported seems to depart from the perfect initial correlation (from February), suggesting, for the future, the need for a more appropriate choice of the sampling point. A better choice and set-up is expected to reduce the problems related to condensation, which is likely to occur at the outlet point where the sampling probe is inserted. Steam condensation would be the responsible for decreasing CO_2 concentration in time.

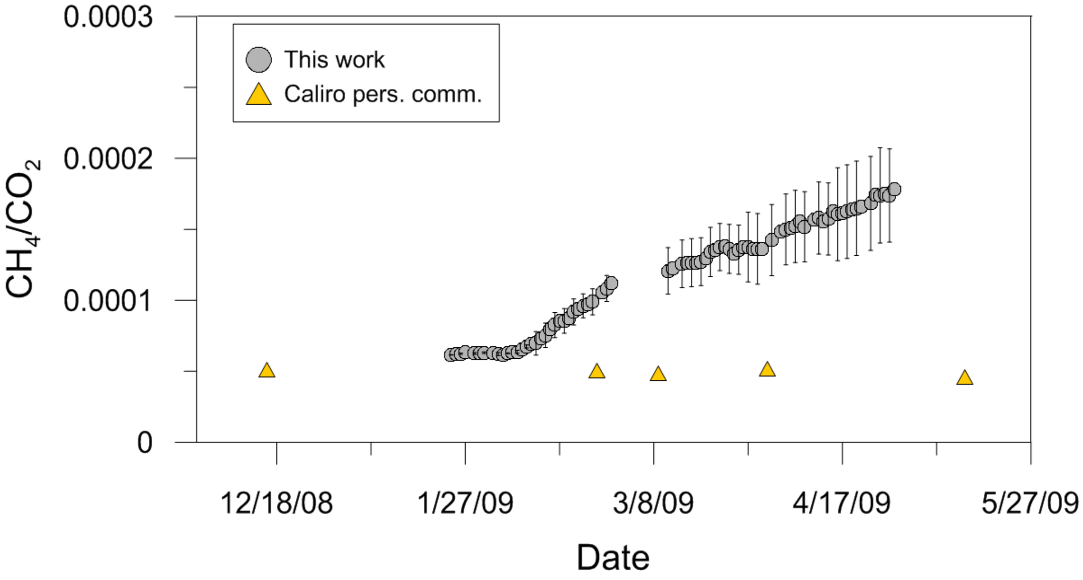

Figure 5. Time series of CH_4/CO_2 ratio at the Pisciarelli fumarole.

Another major species prevailing in geothermal fluid phase gas reactions [Giggenbach, 1980] is H_2S. Our H_2S/H_2 ratio values (ranged from ~2 to ~3) are similar to the average (~2.4) shown in other authors' samples (Caliro pers. comm., Fig. 6). Also in this case, from March 2009, our H_2S/H_2 values decrease by departing from other discrete-samples dataset. Similarly, He/CO_2 ratio values, from March 2009, show a deviation compared to our first results, and from the descrete-samples (Fig. 7).

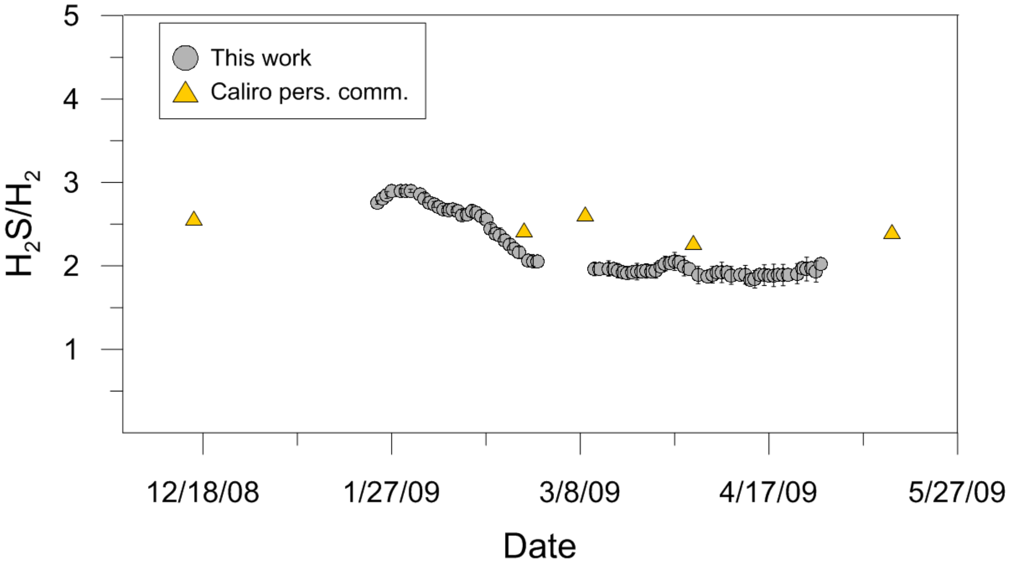

Figure 6. Time series of H_2S/H_2 ratio at the Pisciarelli fumarole.

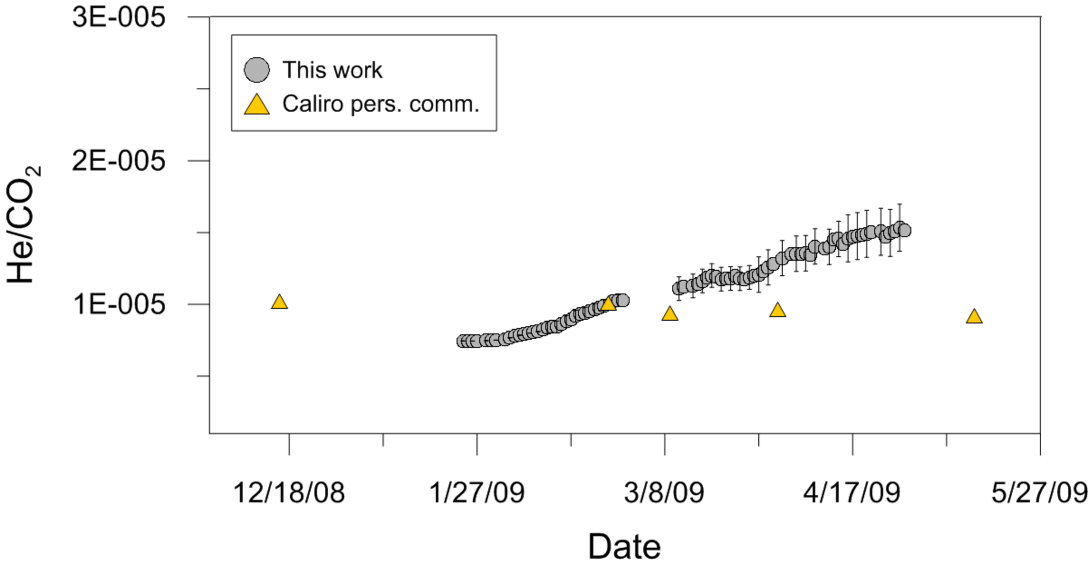

Figure 7. Time series of He/CO_2 ratio at the Pisciarelli fumarole.

In 2012 the same He/CO_2, H_2S/H_2 and CH_4/CO_2 ratios and H_2/CH_4 values were plotted (Figs. 8-11). The ratios measured, show significant variations. In this case, our data seem to be far more distant from the discrete-samples analysis of our reference authors, and suggest that, during the campaign in 2012, a new sampling point for our method was less not appropriate and it has worsened the problem of condensation removal.

The CH_4/CO_2 ratio (Fig. 8) values suggest a CO_2 loss driven by its solubility in condensed steam (e.g., Giggenbach [1980]). In addition, the data suggest also an excess of CH_4 (Fig. 8) and H_2 (Figs. 9 and 10).

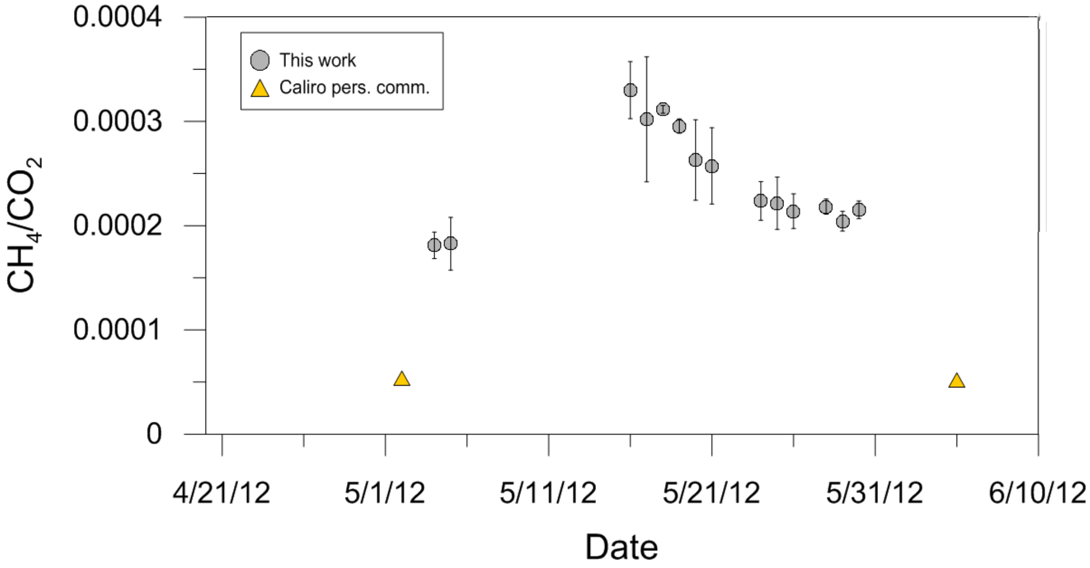

Figure 8. Time series of CH_4/CO_2 ratio at the Pisciarelli fumarole.

It is worth noting that at the beginning of the 2012 campaign, the H_2/CH_4 ratio (Fig. 9) is in line with the other reference-data. Afterward, we suspect the possible formation, at these temperatures and with high H_2O concentration, of an extremophile organism colony. This would have in fact found optimal cfor its development at a depth of ~10-15 cm, which is the same depth of sampling probe point during the 2012 campaign. We infer such a process to be responsible for anomalous H_2 and CH_4 values.
At the beginning of the 2012 campaign, the H_2/CH_4 ratio (Fig. 9) is in line with the other reference-data, but then we believe we added a further aggravating factor, as could also be a possible formation, at those temperatures, and with high H_2O concentration, the development of optimum environment for a extremophile organism colony, able to adapt to those conditions and at a depth of ~10-15 cm (the same depth of sampling probe point in 2012 campaign).

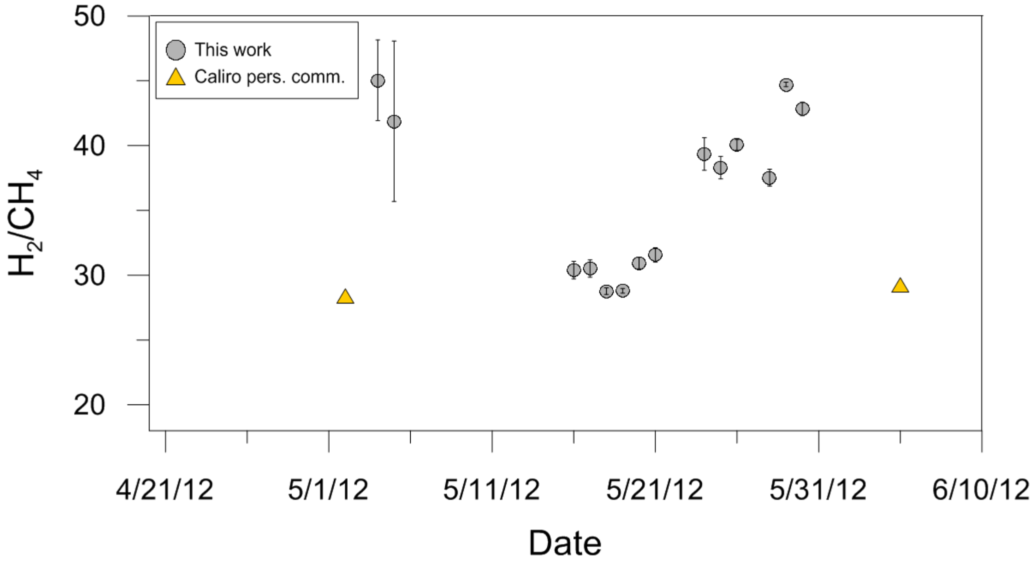

Figure 9. Time series of H_2/CH_4 ratio at the Pisciarelli fumarole.

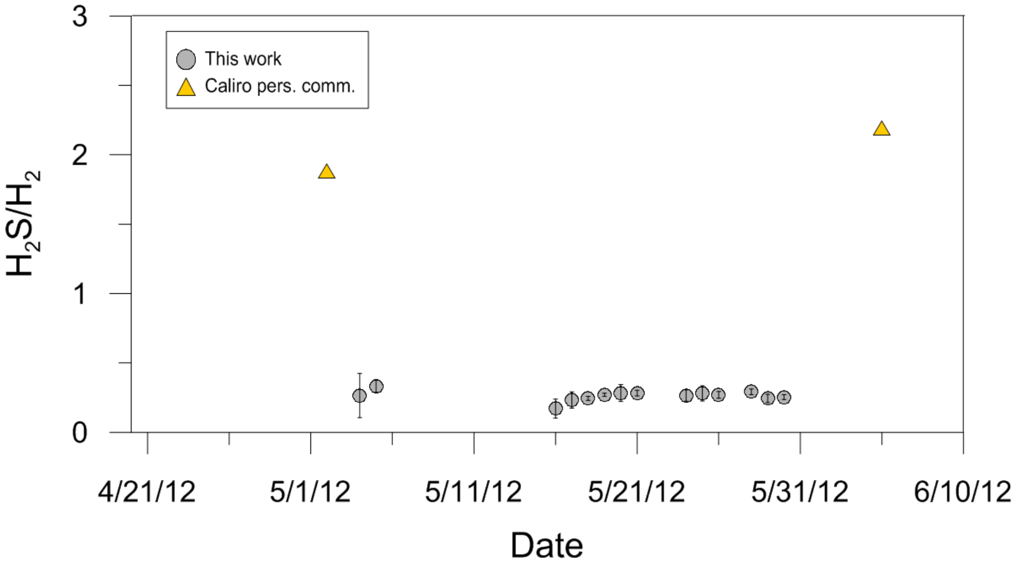

Figure 10. Time series of H_2S/H_2 ratio at the Pisciarelli fumarole.

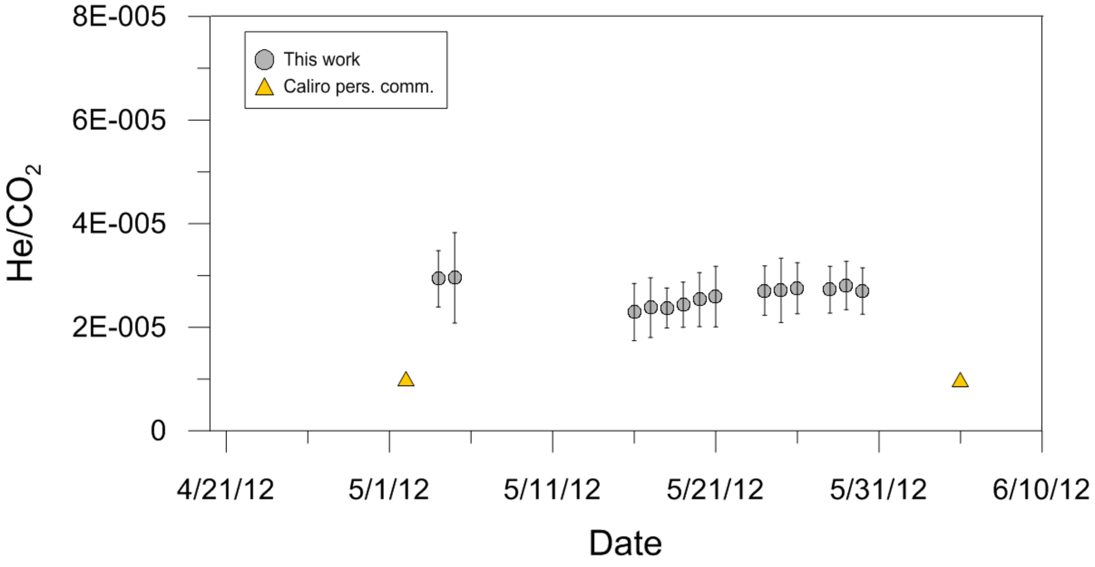

Figure 11. Time series of He/CO_2 ratio at the Pisciarelli fumarole.

Finally, figure 11 shows the He/CO_2 ratio values, compared to the discrete-samples (two values in January and June 2012), which seem to be in line with the other reference-data, if higher than the average ($1.002 \cdot 10^{-5}$).

6. Conclusions

In this preliminary work we present an innovative system for in-situ monitoring of several parameters, such as the concentration of selected gas species, detected at the Pisciarelli fumarolic emission at short time intervals with a quadrupole mass spectrometer (QMS). This first experiment was a test for demonstrating the potential of QMS measurements for volcanic gas monitoring.

Although not all existing problems (blocked pipes, sensor stability and power supply) have been solved, we would continue its technical development. The major problem that we faced was the condensation of water inside the gas extraction device due to the large amount of water vapour discharged from the fumarole. In 2009, our results are comparable to the "classical" sampling methods, but the results are more amplified for the most insoluble species. This is due to a greater precaution to be applied, in the future, to improve water reduction in the sampling-line. Especially in 2012, the comparability of our data with other authors is partial. Certainly this is a method that allows a high sampling rate, comparable, in the future, with geochemical data and geophysical aspects of the area.

Nevertheless, this methodology of continuous monitoring, which provides additional information e.g. on short-term gas variations than the traditional sampling, allowed us to acquire more frequent data of gas composition in the fumarolic area of Pisciarelli and demonstrated that observing significant short/medium-term geochemical signals, at volcanic-hydrothermal system, is possible.

In conclusion, we believe in the opportunity to develop automatic system of measurements to be installed in the field, and, even if the presented results must be still further validated, new experiments can be performed (starting with the choice of the sampling gas point) better refining this technique.

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