



# Hydrogen sulfide measurements in air by passive/diffusive samplers and high-frequency analyzer: A critical comparison



S. Venturi <sup>a, b, \*</sup>, J. Cabassi <sup>a, b</sup>, F. Tassi <sup>a, b</sup>, F. Capecchiacci <sup>a, b</sup>, O. Vaselli <sup>a, b</sup>, S. Bellomo <sup>c</sup>, S. Calabrese <sup>d</sup>, W. D'Alessandro <sup>c</sup>

<sup>a</sup> Dipartimento di Scienze della Terra, University of Florence, Via G. La Pira 4, 50121 Florence, Italy

<sup>b</sup> CNR – Istituto di Geoscienze e Georisorse, Via G. La Pira 4, 50121 Florence, Italy

<sup>c</sup> Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Via Ugo La Malfa 153, 90123 Palermo, Italy

<sup>d</sup> Dipartimento di Scienze della Terra e del Mare, University of Palermo, Via Archirafi 36, 90123 Palermo, Italy

## ARTICLE INFO

### Article history:

Received 10 February 2016

Received in revised form

23 May 2016

Accepted 6 July 2016

Available online 7 July 2016

### Keywords:

Active analyzers

Passive/diffusive samplers

Gaseous contaminants

Air quality monitoring

Hydrogen sulfide

## ABSTRACT

In this study, hydrogen sulfide (H<sub>2</sub>S) measurements in air carried out using (a) passive/diffusive samplers (Radiello<sup>®</sup> traps) and (b) a high-frequency (60 s) real-time analyzer (Thermo<sup>®</sup> 450i) were compared in order to evaluate advantages and limitations of the two techniques. Four different sites in urban environments (Florence, Italy) and two volcanic areas characterized by intense degassing of H<sub>2</sub>S-rich fluids (Campi Flegrei and Vulcano Island, Italy) were selected for such measurements. The concentrations of H<sub>2</sub>S generally varied over 5 orders of magnitude (from 10<sup>-1</sup>–10<sup>3</sup> μg/m<sup>3</sup>), the H<sub>2</sub>S values measured with the Radiello<sup>®</sup> traps (H<sub>2</sub>S<sub>R</sub>) being significantly higher than the average values measured by the Thermo<sup>®</sup> 450i during the trap exposure (H<sub>2</sub>S<sub>Ta</sub>), especially when H<sub>2</sub>S was <30 μg/m<sup>3</sup>. To test the reproducibility of the Radiello<sup>®</sup> traps, 8 passive/diffusive samplers were contemporaneously deployed within an 0.2 m<sup>2</sup> area in an H<sub>2</sub>S-contaminated site at Mt. Amiata (Tuscany, Italy), revealing that the precision of the H<sub>2</sub>S<sub>R</sub> values was ±49%. This large uncertainty, whose cause was not recognizable, is to be added to that related to the environmental conditions (wind speed and direction, humidity, temperature), which are known to strongly affect passive measurements. The Thermo<sup>®</sup> 450i analyzer measurements highlighted the occurrence of short-term temporal variations of the H<sub>2</sub>S concentrations, with peak values (up to 5732 μg/m<sup>3</sup>) potentially harmful to the human health. The Radiello<sup>®</sup> traps were not able to detect such temporal variability due to their large exposure time. The disagreement between the H<sub>2</sub>S<sub>R</sub> and H<sub>2</sub>S<sub>Ta</sub> values poses severe concerns for the selection of an appropriate methodological approach aimed to provide an accurate measurement of this highly toxic air pollutant in compliance with the WHO air quality guidelines. Although passive samplers may offer the opportunity to carry out low-cost preliminary surveys, the use of the high-frequency H<sub>2</sub>S analyzer is preferred when an accurate assessment of air quality is required. In fact, the latter provides precise real-time measurements for a reliable estimation of the effective exposure to hazardous H<sub>2</sub>S concentrations, giving insights into the mechanisms regulating the dispersion of this air pollutant in relation to the meteorological parameters.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Air pollution is the top environmental risk factor for premature death in Europe (EEA, 2014). The development of efficient methodologies to: (i) monitor the behavior and fate of air pollutants, (ii)

identify the contaminant sources and (iii) evaluate the hazard for human health and environment, is a primary issue in environmental monitoring. The most broadly applied technique for monitoring air pollutants, including H<sub>2</sub>S, NO<sub>2</sub>, O<sub>3</sub>, Hg, benzene, toluene, ethylbenzene and xylene (BTEX), involves the use of passive/diffusive samplers (e.g. Shooter et al., 1995; Flores et al., 1996; Bernard et al., 1999; Tang et al., 2002; Klánová et al., 2006; Campos et al., 2010; Nash and Leith, 2010; Zabiegala et al., 2010; Byanju et al., 2012; Colomer et al., 2012; D'Alessandro et al., 2013;

\* Corresponding author. Department of Earth Sciences, Via G. La Pira 4, 50121, Florence, Italy.

E-mail address: [stefania.venturi@unifi.it](mailto:stefania.venturi@unifi.it) (S. Venturi).

Pavilonis et al., 2013; Al-Awadhi, 2014; Huang et al., 2014). These devices consist of a tube packed with a specific adsorbent able to trap the pollutant diffusing through the tube according to Fick's First Law (i.e. gas molecules move from high to low concentration zones). The low cost and no power supply requirement of the passive traps allow their use at multiple locations, in order to easily obtain a general view about the spatial distribution of the air pollutant (Hangartner, 2000). However, this method implies a relatively long exposure time (up to several days), preventing the detection of short-term temporal variations (faster than the exposure time) of the pollutant concentrations (Krupa and Legge, 2000). In addition, the efficiency of the traps is strongly affected by several environmental factors, e.g. temperature, humidity and wind speed (Brown, 2000; Krupa and Legge, 2000; Delgado-Saborit and Esteve-Cano, 2006), whose effects are difficult to quantify. Analytical instruments equipped with high-sensitivity detectors have successfully been used to provide active (i.e. collecting air samples by a pump set at a specific flow rate) measurements of various air pollutants at high temporal frequency, such as CO<sub>2</sub>, H<sub>2</sub>S, SO<sub>2</sub>, NO<sub>x</sub> and O<sub>3</sub> (e.g. Carapezza et al., 1984; Badalamenti et al., 2001; Kourtidis et al., 2004; Peralta et al., 2013; Olafsdottir et al., 2014). Nevertheless, this approach is generally expensive and requires frequent instrument calibration and an *in situ* power source available.

Selecting the most appropriate technique for measuring air pollutant concentration requires consideration of the trade-offs between advantages and limitations of passive and active methods which have to be carefully evaluated. Accordingly, the present study focused on the comparison between two different analytical approaches: a) Radiello<sup>®</sup> traps and b) a Thermo<sup>®</sup> 450i analyzer, to measure hydrogen sulfide (H<sub>2</sub>S) concentrations in air. Indoor and outdoor H<sub>2</sub>S measurements in a wide concentration range were performed in areas characterized by both natural and anthropogenic H<sub>2</sub>S sources. The main aim was to evaluate the reliability and the efficiency of the two techniques for investigating and monitoring this air pollutant in compliance with the ambient air quality standards dictated by the World Health Organization (WHO, 2000, 2003).

## 2. Origin of hydrogen sulfide (H<sub>2</sub>S) and its impact on human health

Hydrogen sulfide is an air pollutant commonly emitted by both natural sources and anthropogenic activity. The latter includes sewage treatment plants, concentrated animal feeding operations, oil and gas refineries, geothermal power plants, paper mills and vehicular traffic (e.g. Kourtidis et al., 2004, 2008; Colomer et al., 2012). Natural H<sub>2</sub>S sources are thermal and cold sulfur-rich springs, wetlands, manure, coal pits, and gas and oil reservoirs (e.g. Bates et al., 1992; WHO, 2003). In particular, huge amounts of H<sub>2</sub>S are emitted from volcanic and hydrothermal systems (e.g. D'Alessandro et al., 2013; Hernández et al., 2015), where this gas may represent a significant hazard for human health (Sigurdsson et al., 2015). For example, in 1971, 1976 and 1997, 13 people were likely asphyxiated by H<sub>2</sub>S emitted from the Kusatsu-Shirane and Adataro volcanoes (Honshu, Japan) (Cook and Weinstein, 2011; Williams-Jones and Reimer, 2015).

Long-term exposures to low H<sub>2</sub>S concentrations can have severe health consequences on respiratory, cardiovascular and nervous systems (e.g. Legator et al., 2001; Bates et al., 2002, 2013). At 15 mg/m<sup>3</sup>, H<sub>2</sub>S provokes eye irritation, while at slightly higher concentrations it induces damage to the upper respiratory tract and causes loss of smell, whereas coma occurs after a single breath when the H<sub>2</sub>S values are ≥1400 mg/m<sup>3</sup> (McManus, 1999; WHO, 2000, 2003).

The maximum allowable concentration of H<sub>2</sub>S for ambient air

reported by the air quality guideline (WHO, 2000) is 150 µg/m<sup>3</sup> (average value in 24 h), although it should not exceed 7 µg/m<sup>3</sup> (average value in 30 min) to avoid significant odor annoyance due to its typical rotten-egg smell (detectable at 0.7–42 µg/m<sup>3</sup>, depending on individual sensitivity; Schiffman and Williams, 2005).

## 3. Methodology

### 3.1. Measurement sites

Measurements of H<sub>2</sub>S concentrations in air were carried out in three different Italian localities (Fig. 1a), i.e. 1) Florence (Tuscany, central Italy; Fig. 1b), an urban context affected by anthropogenic H<sub>2</sub>S sources, 2) Solfatara crater (Fig. 1c), a tuff cone in Campi Flegrei showing an intense fumarolic activity and strong diffuse soil gas emission (e.g. Caliro et al., 2007; Tassi et al., 2013) and 3) Vulcano Island in the Aeolian Archipelago (Fig. 1d), where S-rich fumaroles occur at the base of the recently active volcanic cone (La Fossa crater) and on the crater rim (e.g. Capaccioni et al., 2001; Granieri et al., 2006).

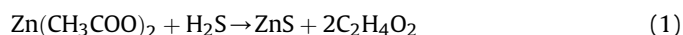
At each site, continuous H<sub>2</sub>S measurements using the Thermo<sup>®</sup> 450i analyzer were carried out during the exposure of the Radiello<sup>®</sup> traps placed at 1.5 m above the ground level and <15 cm away from the analyzer. The exposure time of the Radiello<sup>®</sup> traps (ranging from 52 to 371 min) was selected on the basis of the real-time measured H<sub>2</sub>S concentrations.

Air temperature, as well as wind speed and direction were measured using a portable Davis Vantage Vue weather station.

A reproducibility test for H<sub>2</sub>S concentrations in air was performed at Mt. Amiata (central Italy; Fig. 1a) by deploying 8 Radiello<sup>®</sup> traps close to each other within an 0.2 m<sup>2</sup> area (Fig. 1e). The selected site was located close to the Acqua Passante well that was drilled for mining exploration in 1938. Presently, it discharges about 1,800, 10 and 0.82 ton/year of CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>S, respectively, from a chimney at about 6 m above the ground level (Nisi et al., 2014) (Fig. 1e). The reproducibility test data of the Radiello<sup>®</sup> traps were compared with those obtained by the simultaneous acquisition of H<sub>2</sub>S measurements at the same site by using the Thermo<sup>®</sup> 450i analyzer.

### 3.2. Radiello<sup>®</sup> traps

The Radiello<sup>®</sup> traps consist of (i) an adsorbent cartridge, (ii) a diffusive body, and (iii) a supporting plate. The polyethylene adsorbent cartridge is placed inside the diffusive body, the latter consisting of a micro-porous high-density polyethylene cylinder connected to the polycarbonate supporting plate. The radial design of the diffusive body optimizes the efficiency of the trap, since it allows the pollutant uptake from all the directions (D'Alessandro et al., 2013; Pavilonis et al., 2013). The adsorbent cartridge is impregnated with zinc acetate [Zn(CH<sub>3</sub>COO)<sub>2</sub>] that reacts with H<sub>2</sub>S producing zinc sulfide (ZnS), according to the following reaction:



Zinc sulfide is then extracted from the cartridge with MilliQ water (10 mL) and analyzed by visible spectrometry after adding 0.5 mL of ferric chloride-amine solution (Fondazione Maugeri, 2007). The H<sub>2</sub>S concentrations in air (H<sub>2</sub>S<sub>R</sub>, in µg/m<sup>3</sup>) are computed according to the following equation (Fondazione Maugeri, 2007):

Download English Version:

<https://daneshyari.com/en/article/6334802>

Download Persian Version:

<https://daneshyari.com/article/6334802>

[Daneshyari.com](https://daneshyari.com)