



Mapping of H₂S fluxes from the ground using copper passive samplers: An application study at the Zolfoforata di Pomezia degassing area (Alban Hills, Central Italy)

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ABSTRACT

A new method for measuring H₂S mass flux from the ground, based on the digital analysis of the interference colours produced by the sulphidation of copper passive samplers (CPS), is proposed and discussed in this article. CPS sulphidation has a wide range of linear responses to H₂S doses and can be used together the accumulation chamber method to estimate gas fluxes from natural degassing areas. These are often characterized by the presence of vent centred degassing areas (VCDAs), which are recognizable from the absence or rarefaction of vegetation due to high acid gas concentrations in the soil pores and in the air at ground level. A reference emission curve, accounting for the advective and diffusive components of the flux, can be modelled and used to estimate the total H₂S mass released from each VCDA. The application of this method can be supported by remote sensing analysis that helps identify VCDAs in the field in perivolcanic H₂S degassing areas.

As an illustrative application, H₂S gas fluxes from the ground were measured in spring 2007 at the Zolfoforata di Pomezia degassing area (ZPDA, Alban Hills, Central Italy) using an accumulation chamber internally equipped with CPS. H₂S peak fluxes were measured over the vents after remote sensing assisted identification of the VCDAs. Further measurements were carried out in two ponds and one artificial channel bordering the study area. The total atmospheric flux released at the ZPDA, estimated to be about 1207.6 kg day⁻¹, was calculated as the summation of the fluxes from all the H₂S sources, the background flux being negligible.

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1. Introduction

Assessing the fluxes of sulphureous gases from the ground released into the atmosphere and knowing their spatial distribution is particularly relevant to the field of geothermometry and volcanology. In general, SO₂, the main sulphur species released by active volcanoes, is emitted directly into the high troposphere, and thus has a global environmental influence (Benkovitz et al., 1997). H₂S, by contrast, is the predominant sulphureous gas emitted by low-temperature perivolcanic degassing areas; this gas may have local-scale effects on the health of the human population (Aiuppa et al., 2005). Since the human respiratory tract is the main target organ of H₂S toxicity, sensitive subpopulations exposed to H₂S are known to suffer from asthma and complicated respiratory function (WHO, 2003). In addition, as H₂S inhibits cytochrome C oxidases, even moderate downwind exposure to H₂S is likely to cause chronic neurobehavioural impairment (Kilburn, 1997).

Studies on H₂S fluxes from the soil in natural degassing areas are rare and relatively recent. At the Teide volcano, Tenerife (Spain),

Salazar et al. (2005) measured CO₂ and H₂S fluxes on the flank of the summit cone, showing that the spatial and temporal variations of such fluxes may provide information on the state of the volcanic system. Ultraviolet spectroscopic studies of H₂S and SO₂ fluxes emitted by the Vulcano, Etna, and Stromboli volcanoes in Italy have shown that H₂S is inert on timescales of seconds to minutes, thus providing an important reference parameter to estimate the volcanic total sulphur budget (Aiuppa et al., 2005). A portable multi-sensor system with electrochemical and infrared sensors was used by Schwandner et al. (2005) to measure CO₂, H₂, CO, and H₂S fluxes in three acid-sulphate sites of the Yellowstone Caldera complex and identify potential sites for hydrocarbon generation in hydrothermal systems. In the NW Peloponnesus petroliferous basin (Greece), Etiope et al. (2005) measured CH₄ and H₂S fluxes during a gas hazard evaluation survey, using the closed chamber method coupled with the sampling of accumulated gas and H₂S analysis by RAE colorimetric tubes. In a biogeochemical study, Xinhua et al. (2007) measured H₂S and COS fluxes from the wetlands of the Sanjiang Plain, in northeastern China, using the static chamber and chromatograph methods, revealing an interesting negative correlation. Lastly, passive samplers to map outdoor H₂S fluxes were used for the area of Rotorua (New Zealand) by Horwell et al. (2005), who successfully tested a method based on colour change associated with the sulphidation of silver bromide salt films.

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In this paper we describe a new, rapid method to measure H₂S concentrations based on the sulphidation of metallic copper passive samplers (CPS) which, when combined with the accumulation chamber method (ACM, Chiodini et al., 1998; Carapezza and Granieri, 2004), yields a reliable direct quantitative assessment of the H₂S mass flux released in a point gas source. The advantages of CPS over silver halide samplers are that CPS do not blacken when they interact with natural light and that they can easily be regenerated by simple scraping.

As an illustrative application, we used this combined CPS/ACM technique to map H₂S fluxes at the Zolforata di Pomezia degassing area (ZPDA), which is located in the western sector of the Alban Hills volcanic complex (Latium, central Italy). The perivolcanic area of the Alban Hills is a zone of major CO₂ and minor H₂S natural degassing (Giggenbach et al., 1988; Carapezza et al., 2005), whose activity has been documented since ancient Roman times and includes the degassing areas of Bagni di Tivoli-Villalba di Guidonia, Ciampino, Pomezia-Palombara, Ardea and Lavinio. H₂S flux from the Alban Hills is a matter of concern owing to the possible negative long-term impact on the health of about 150,000 residents (Chiodini and Frondini, 2001; Voltaggio et al., 2001a; Pizzino et al., 2002; Annunziatellis et al., 2003; Carapezza et al., 2003; Beaubien et al., 2003; Voltaggio, 2004). Apart from these environmental aspects, the measurement of spatial and temporal H₂S flux changes in a natural degassing area belonging to a quiescent active volcano (Carapezza and Tarchini, 2007) may also help to estimate the mean rising time (MRT) of the gas from its source to the surface (Voltaggio et al., 1998). This is a key parameter for predicting the temporal delay between seismic activity and paroxysmal gaseous surface manifestations.

2. Materials and methods

2.1. Copper based passive samplers

2.1.1. Copper sulphidation

Copper sulphidation has been studied in detail by Graedel et al. (1983) and, more recently, by Barbour et al. (2002). The overall chemical reaction describing this process is:



However, the real process consists of two distinct reactions:



Four different phases follow one another when metallic copper is exposed to H₂S-rich atmosphere (Voltaggio, 2004):

- 1) reaction with oxygen and formation of a 2–4 nm thick film of copper oxide covered by adsorbed water;
- 2) formation of chalcocite (Cu₂S) “islands” at the copper oxide-adsorbed water boundary;
- 3) inward formation and linear thickening of a continuous film of Cu₂S and consumption of the copper oxide film;
- 4) H₂S diffusion through the metallic copper, after the formation of about 150 nm of Cu₂S, and thickening of copper sulphide with a parabolic trend over time.

2.1.2. Sulphidation and measurement of Cu₂S thickening: AEL method

During the afore-mentioned phases 2) and 3), namely during the formation of a 2 to 150 nm layer of Cu₂S, the thickening remains linear over time and, when time is equal, it remains linear over a wide H₂S concentration range. In order to test this linearity, we implanted ²¹²Pb ions onto copper bar surfaces using a thoron implantation chamber described by Voltaggio et al. (2001b).

According to the α-particle energy loss method (AEL) described by Kelson et al. (1995), the energy decrease in the alpha particles emitted by the two radionuclides of ²¹²Pb progeny (²¹²Bi and ²¹²Po) can be measured by α-spectrometry before and after sulphidation at different H₂S doses. Measurement of the alpha energy decrease in MeV, combined with the known value of chalcocite density, can be used to calculate the mean thickness of Cu₂S film.

CPS, similarly to the other gas passive samplers, record the H₂S dose, i.e. $D_{\text{H}_2\text{S}}$, to which they are exposed. $D_{\text{H}_2\text{S}}$, expressed in ppmv·sec, is equal to:

$$D_{\text{H}_2\text{S}} = C \cdot E \quad (4)$$

where C is the H₂S concentration in ppmv and E is the exposure time in seconds. Ten sulphidized copper bars implanted with ²¹²Pb yield a linear trend between Cu₂S thickness and $D_{\text{H}_2\text{S}}$ within a 100 nm thickness range (Fig. 1), with a mean sulphidation rate of about 0.0024 nm ppmv⁻¹ s⁻¹ (Voltaggio, 2004).

The use of the AEL method for estimating $D_{\text{H}_2\text{S}}$, based on the measurement of the thickness of Cu₂S films on copper bars, not only requires a considerable amount of time for the preparation of the alpha emitted layer and measurement of alpha energies, but is also intrinsically limited by the half-life of the implanted ²¹²Pb (about 12 h). Consequently, the AEL method is not suitable for a systematic field study during which a high number of samples have to be taken and measured in the laboratory. We therefore focused on the light interference produced by the growth of a chalcocite film on copper bars, which can be measured far more easily.

2.1.3. Copper sulphidation and light interference

The formation of a Cu₂S nanometric film over Cu₂O produces interference phenomena of the light reflected by the two surfaces that depend on the thickness (d) of the chalcocite film. The Cu₂S refractive index for any wavelength of visible light, ranging between 1.8 and 2.0 (Gadgil et al., 1987), is lower than the refractive index of underlying Cu₂O. In this specific case, the theory of thin-film interference of natural light (Vazquez-Santoyo et al., 2005) states that a maximum of destructive interference occurs when:

$$d = \frac{(2m+1) \cdot \lambda}{4n} \quad (5)$$

whereas a maximum of constructive interference is observed when :

$$d = \frac{m \cdot \lambda}{2n} \quad (6)$$

where d is the thickness of the upper film, λ is the incident wavelength, m is the interference order and n is the refractive index of the upper film.

Since both destructive and constructive interferences vary for each wavelength of natural light as the film becomes thicker, the colour of the copper bar progressively changes within the range of the first order interference colours of Newton's series: faint yellow, orange red, indigo, blue, green, grey. This colour sequence is not a spectrum but progressively appears as the thickness of the film increases. During the first stages of sulphidation, the discontinuity of the chalcocite islands on the copper surface produces a visible colour that is a mixture between the expected interference colour and the natural pink colour of the copper bar. The subsequent formation of a nearly continuous film yields visible colours that are increasingly similar to the standard ones predicted by the interference theory (Fig. 2a). For example, a reddish to violet colour is expected when the film thickness is around 120 nm, which is attained when the copper bar has been exposed to a H₂S dose of 50,000 ppmv s.

Since the film thickness of the neo-formed chalcocite is directly related to the dose, it is possible to calibrate this process in the lab in order to calculate the dose on the basis of the colour.

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