



Soil processes modify the composition of volatile organic compounds (VOCs) from CO₂- and CH₄-dominated geogenic and landfill gases: A comprehensive study

A. Randazzo^{*}, S. Venturi, F. Tassi

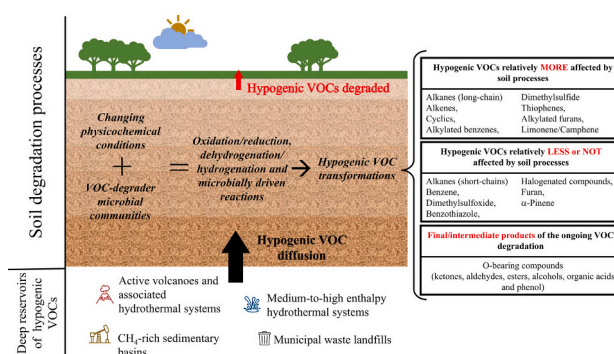
Department of Earth Sciences, University of Florence, Via G. La Pira 4, 50121 Firenze, Italy

Institute of Geosciences and Earth Resources (IGG), National Research Council of Italy (CNR), Via G. La Pira 4, 50121 Firenze, Italy

HIGHLIGHTS

- The composition of hypogenic gases depends on the genetic environment conditions.
- Hypogenic light, non-alkylated and oxidised compounds are favoured in the soil.
- Hypogenic heavy and alkylated species are preferentially degraded in the soil.
- Soil processes are (co-)metabolic/hydrogenation/dealkylation/oxidation reactions.
- They depend on local soil conditions and not on the CO₂ and CH₄ flux values.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Jose Julio Ortega-Calvo

Keywords:

VOC
Biogeochemical process
Landfill
Geogenic system
Soil gas
Gas vent

ABSTRACT

Degradation mechanisms affecting non-methane volatile organic compounds (VOCs) during gas uprising from different hypogenic sources to the surface were investigated through extensive sampling surveys in areas encompassing a high enthalpy hydrothermal system associated with active volcanism, a CH₄-rich sedimentary basin and a municipal waste landfill. For a comprehensive framework, published data from medium-to-high enthalpy hydrothermal systems were also included. The investigated systems were characterised by peculiar VOC suites that reflected the conditions of the genetic environments in which temperature, contents of organic matter, and gas fugacity had a major role. Differences in VOC patterns between source (gas vents and landfill gas) and soil gases indicated VOC transformations in soil. Processes acting in soil preferentially degraded high-molecular weight alkanes with respect to the low-molecular weight ones. Alkenes and cyclics roughly behaved like alkanes. Thiophenes were degraded to a larger extent with respect to alkylated benzenes, which were more reactive than benzene. Furan appeared less degraded than its alkylated homologues. Dimethylsulfide was generally favoured with respect to dimethylsulfide. Limonene and camphene were relatively unstable under aerobic conditions, while α -pinene was recalcitrant. O-bearing organic compounds (i.e., aldehydes, esters, ketones, alcohols, organic acids and phenol) acted as intermediate products of the ongoing VOC degradations in soil. No evidence for the degradation of halogenated compounds and benzothiazole was observed. This study

^{*} Corresponding author at: Department of Earth Sciences, University of Florence, Via G. La Pira 4, 50121 Firenze, Italy.

E-mail address: antonio.randazzo@unifi.it (A. Randazzo).

<https://doi.org/10.1016/j.scitotenv.2024.171483>

Received 10 October 2023; Received in revised form 6 February 2024; Accepted 3 March 2024

Available online 7 March 2024

0048-9697/© 2024 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

pointed out how soil degradation processes reduce hypogenic VOC emissions and the important role played by physicochemical and biological parameters on the effective VOC attenuation capacity of the soil.

1. Introduction

Non-methane volatile organic compounds (hereafter VOCs) have received growing attention from the scientific community as well as from intergovernmental and national organisations. Multiple lines of evidence have highlighted that most VOCs pose detrimental effects on the surface environment (Chen et al., 2020), atmospheric chemistry (Kansal, 2009), air quality (Conti et al., 2020; Gallego et al., 2012) and human health (Gostner et al., 2016; Montero-Montoya et al., 2018).

VOCs, originating from (1) biogenic, (2) geogenic, and (3) anthropogenic sources, are ubiquitous in Earth's natural systems and accumulate in the atmosphere due to their high volatility and relatively low affinity with liquids and solids (Koppmann, 2020).

Biogenic VOCs, accounting for about 90 % of the total annual VOC load in air (Unger, 2014), mainly consist of isoprene and monoterpenes, and include relatively low amounts of aliphatic O-substituted compounds (esters, alcohols, aldehydes, ketones and ethers), alkanes, alkenes, aromatics and sesquiterpenes (Guenther, 1995). They are synthesised by vegetative parts of woody plants, flowers, fruits, leaves and roots and derive from the biodegradation of biomass in soil (Greenberg et al., 2012; Lun et al., 2020; Tang et al., 2019).

Geogenic VOCs are related to (i) volcanic and hydrothermal CO₂-dominated degassing and (ii) CH₄-dominated seepages from deep oil and natural gas deposits (Bonini et al., 2013; Tassi et al., 2013a). Even though significant amounts of alkane, alkene, aromatic, cyclic, halogenated and heteroatomic (e.g., O-, N-, and S-substituted) compounds have been revealed in deep-sourced gas vents (e.g., Ricci et al., 2023; Schwandner et al., 2004; Tassi et al., 2015a, 2012c), data concerning the broad spectrum of VOCs in geogenic fluids is still incomplete and scarce. As a result, conceptual models describing global atmospheric VOC budgets generally neglect geogenic contributions (Frische et al., 2006; Guenther et al., 2000; Vichi et al., 2021). Geogenic VOCs are mostly produced by thermal and microbially driven degradation processes of organic matter embedded in rocks, whilst abiogenic VOC production is still debated (McCollom and Seewald, 2006; Tassi et al., 2012c, 2012d). Geogenic gases are released into the atmosphere through (i) open vents (e.g., fumaroles, bubbling pools, mud volcanoes and macroseepages), which are related to the advective mechanism in which the transport of gas occurs through highly permeable structures including fractures, joints or faults by pressure gradients (Chiodini et al., 1998; Chiodini and Frondini, 2001; Taussi et al., 2021) and (ii) diffuse degassing from soils, consisting of relatively slow gas release from permeable routes within the soil towards the surface in response to concentration gradients (i.e., diffusive mechanism; Etiope and Martinelli, 2002).

The contribution of anthropogenic VOCs to the global atmospheric VOC budget is still uncertain and reliable estimates are lacking so far (Goldstein and Shaw, 2003), although it is expected to be significantly lower than that derived from biogenic processes (Duan et al., 2023; Messina et al., 2016). Nevertheless, anthropogenic VOCs are raising a growing interest caused by their strong impacts on air quality, at both local (Crippa et al., 2021; Knox, 2005; Lewis, 2018; Sonne et al., 2022; Wei et al., 2008) and global scale (Unger, 2014; Yáñez-Serrano et al., 2020). Industry, on-road and off-road transport, biomass burning, power plants and waste treatment facilities have been recognised as the largest anthropogenic VOC emitters (Gu et al., 2021; Keita et al., 2018; Waked et al., 2016). Among these sources, municipal waste landfills deserve special mention. CH₄ emissions from municipal waste landfilling, accounting for about 18 % of the global anthropogenic CH₄ emissions (Huang et al., 2022a), are expected to grow by around 12 % by 2050 (Global Methane Initiative, 2023). Besides CH₄, landfill emissions, being lost from pipe collection systems and permeating through cover soil

(Fredenslund et al., 2010), include significant amounts of different polluting and odorigenous VOCs, mostly consisting of alkanes and aromatics with minor alkene, cyclic, halogenated, terpene, O- and S-substituted compounds (Duan et al., 2021; Gao et al., 2021; Nair et al., 2019).

The rapid uprising of hypogenic gases (i.e., geogenic and landfill gas) up to the surface through highly permeable fractures within soils (advection mechanism) limits the VOC degradation operated by secondary processes (Tassi et al., 2015a, 2015b). In contrast, during slow uprising (diffusive mechanism) through low permeable soil, the hypogenic VOCs, sensitive to physicochemical conditions, are strongly degraded (Giggenbach, 1996; Pallasser, 2000; Randazzo et al., 2020; Schwandner et al., 2004, 2013; Tassi et al., 2012c). Typical VOC degradation processes are (i) dissolution in soil pore water, (ii) absorption on/in soil particles (Asensio et al., 2007; Nyrop Albers et al., 2018; Tang et al., 2019), (iii) hydration/dehydration, and (iv) oxidation/reduction processes (Shock et al., 2013). Moreover, VOCs can be affected by biological processes carried out by a wide variety of microorganisms (Abbasian et al., 2015; Alvarez-Cohen and McCarty, 1991; Alvarez-Cohen and Speitel, 2001; Chaignaud et al., 2018; Cleveland and Yavitt, 1997; Hanson and Hanson, 1996; Kjeldsen et al., 1997; Koh et al., 1993; Lee et al., 2011; Rojo, 2009; Van Beilen and Funhoff, 2007).

Insights into shallow biogeochemical soil processes acting on VOCs are mostly provided by laboratory experiments, generally carried out by using pure cultures and a few selected different VOCs under fixed conditions (Boopathy, 2004; Brown et al., 2021; Kadri et al., 2021; Zuo et al., 2022), with no validation with field measurements. Such an approach has strong limitations for the prediction of VOC biodegradation in soils, due to the unpredictable development of different microbial communities and chemical reactions. As a result, the behaviour at shallow depths of hypogenic VOCs from hydrothermal/volcanic areas, hydrocarbon-bearing sedimentary basins, and landfills is still poorly understood.

The main aim of this study was to investigate the effect of biogeochemical processes occurring within the soil on the composition of hypogenic VOCs in CO₂- and CH₄-dominated gases from medium-to-high enthalpy to volcanic systems and municipal waste degradation, in relation to: (i) the gas flux, i.e., the residence time of gases at shallow depths; (ii) redox conditions, i.e., O₂ contents; (iii) the composition of the source gases. Insights into the genetic processes of VOCs in these geogenic and anthropogenic systems were also provided. The study was based on original data encompassing different geochemical parameters, including CO₂ (Φ_{CO_2}) and CH₄ (Φ_{CH_4}) diffuse fluxes from the soil, and the composition of organic and inorganic interstitial soil gases along vertical profiles within soils. Gas samples were collected from four study areas located in Italy, belonging to peculiar environmental contexts: (i) an active volcano and the associated high enthalpy hydrothermal system, i.e., Vulcano Island (the Aeolian Archipelago, southern Italy); (ii) a CH₄-rich sedimentary basin, i.e., Terre Calde di Medolla (Modena, central Italy) and (iii) a municipal waste landfill, i.e., Belvedere Inc. landfill sited in Peccioli (Pontedera, Pisa, central Italy). Published data of gases from medium-to-high enthalpy hydrothermal systems, i.e., (i) Solfatara di Nepi and Caldara di Manziiana (central Italy; Venturi et al., 2024), Solfatara crater (southern Italy; Tassi et al., 2015a) and Poggio dell'Ulivo (central Italy; Tassi et al., 2015b), were included.

2. Study sites

2.1. Vulcano Island

Vulcano Island is the southernmost volcanic edifice of the Aeolian

archipelago located approximately 25 km N of the Sicilian coast (southern Italy) (Fig. 1). The Aeolian archipelago is the result of the back-arc volcanism related to the subduction of the Ionian plate beneath the Tyrrhenian Sea (Polonia et al., 2011). Currently, Vulcano Island is a closed-conduit volcano characterised by intense fumarolic activity, mostly occurring at Baia di Levante (hereafter, BdL; Fig. 1a) and the top of the northern flank of the La Fossa crater (hereafter, LFC; Fig. 1b) (Baubron et al., 1990). Gases discharged from LFC are characterised by temperatures up to 400 °C and a typical magmatic-derived composition (i.e., $H_2O > CO_2 > H_2S/SO_2 > HCl > HF$; Chiodini et al., 1993) originating from the interaction of fluids from magmatic degassing with a shallow aquifer partially fed by seawater (Carapezza et al., 1981; Chiodini et al., 1995). Fluids discharged from BdL, characterised by temperatures close to that of boiling water at atmospheric pressure (Chiodini et al., 1995), are inferred to originate from multilevel boiling aquifers heated by magmatic fluids (Diliberto et al., 2021; Sommaruga, 1984). As a result, BdL exhalations are dominated by H_2O and CO_2 with relatively high contents of CH_4 , and the absence of acidic gases (i.e., SO_2 , HCl and HF) that dissolve into the hydrothermal reservoirs before reaching the surface (Capaccioni et al., 2001; Capasso et al., 1997; Chiodini et al., 1995).

Given the high temperature characterising both the magmatic and

hydrothermal fluid reservoirs, VOCs emitted from LFC and BdL fluid discharges are commonly ascribed to thermogenesis rather than biogenesis, whilst the supply from abiogenic processes is still not clear (Schwandner et al., 2004, 2013; Tassi et al., 2012c).

2.2. Terre Calde di Medolla

“Terre Calde di Medolla” (literally “Hot Lands of Medolla”; hereafter, TCM) is a local name used for describing a farming field area ($< 0.5 \text{ km}^2$) located within the southern sector of the Po River plain (northern Italy) and characterised by ground temperatures up to 51.8 °C (Sciarrà et al., 2021) (Fig. 1c). TCM exhibits discrete subcircular CH_4 -dominated seepages ($< 5 \text{ m}$ diameter) marked by the lack of healthy vegetation and the presence of a clay-altered cover. The anomalous heating of the ground is ascribed to the massive exothermic oxidation of CH_4 to CO_2 by methanotrophic bacteria in the shallower soil layers (Capaccioni et al., 2015; Cappelletti et al., 2016). TCM lies at about 10 m above the thrust-ramp anticline Mirandola thrust (Boccaletti et al., 2011; Paolucci et al., 2015; Tarabusi and Caputo, 2017) that belongs to the most external active fold-and-thrust system named Ferrara arc (Turrini et al., 2015, 2016); the last is the outermost front of the NNE-verging Northern Apennine belt (Maesano et al., 2015). The stratigraphic logs provided by

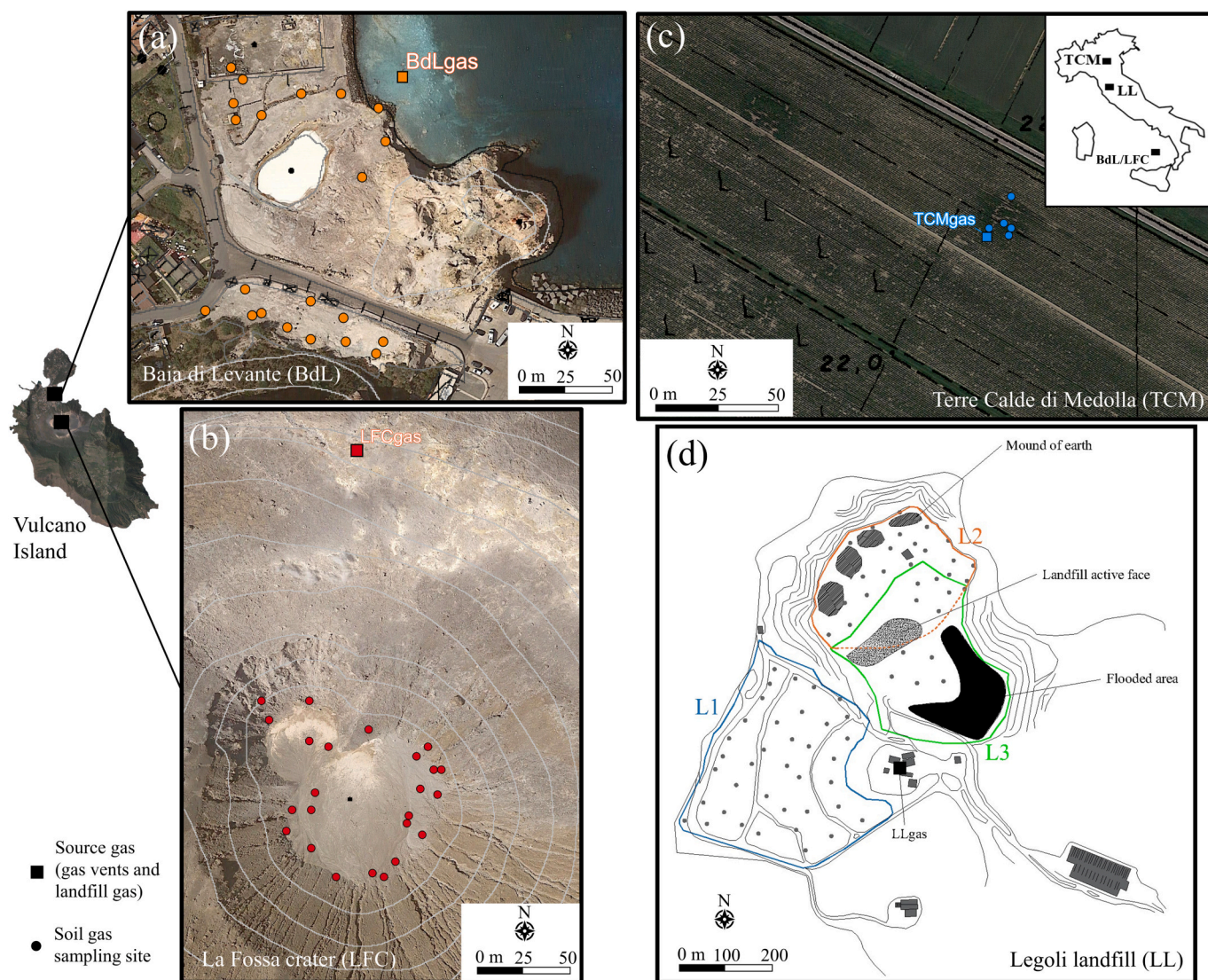


Fig. 1. Location of sampling sites in Vulcano Island i.e., (a) Baia di Levante (BdL) and (b) La Fossa crater (LFC), (c) Terre Calde di Medolla (TCM) and (d) Legoli landfill (LL).

three nearby (within 1.5 km) deep boreholes (i.e., Camurana 001 drilled in 1943, Bignardi 001 drilled in 1933, and Bignardi 001 DIR BIS drilled in 1944; ViDEPI, 2022) have revealed occurrences of discontinuous natural gas reservoirs at about 700 m depth and from 2100 to 2650 m depth in the correspondence of brackish-marine deposits and the existence of intense faulting systems related to the tectonic stresses from which gases can preferentially migrate upwards (Capaccioni et al., 2015).

Given the low thermal gradients characterising the Po plain area (15–30 °C/km; Viganò et al., 2012), TCM gases are generally interpreted as biogenic, whilst thermogenic contribution from the Mesozoic succession at depths >3000 m have been solely hypothesised (Capaccioni et al., 2015; Sciarra et al., 2017).

2.3. Legoli landfill

The municipal waste landfill of Legoli (hereafter, LL) is located in Peccioli (Province of Pisa, central Italy) (Fig. 1d). Overall, LL covered a surface area of 340,000 m² and consisted of three main independent cells (Fig. 1d): (i) cell I (L1), with a total surface area of about 140,000 m², closed in 2007, which received a total of about 3.1 million ton of municipal waste, (ii) cell II (L2), more recent and not exploited at the time of the sampling campaigns, which extended for approximately 53,000 m², and (iii) the exploited cell III (L3), partly overlapped to L2, having a total surface area of about 126,000 m². The closed L1 cell was provided with a final cover consisting upwards of clay, soil and grassing, whilst both the L2 and L3 cells were equipped with a thinner provisional cover constituted by only soil. The covering soil was generally obtained from the excavated clay materials derived from cuts for the construction of the landfill itself, amended with variable proportions of bio-stabilised organic fraction of municipal waste, sludge or allochthonous soils. A total of about 300,000 tons of waste was yearly disposed of at LL, including: (i) undifferentiated municipal waste (ca. 60 % of the total disposed of waste); (ii) waste materials for amending definitive/provisional/daily soil covers including the bio-stabilised organic fraction of municipal waste, sludge, reclaimed land and excavated soils (ca. 40 %), and (iii) tyres (ca. 10⁻³ %).

3. Materials and methods

3.1. Sampling strategy

The number of sampling sites for interstitial soil gas collection was commensurate with the extension of the diffuse degassing areas, whilst their locations were selected to provide a complete scan of the study areas. To investigate whether redox conditions influence soil degradation processes, soil gases were collected at two levels along vertical profiles in which the shallow one is expected to be more oxidising than the deep one, as follows: (i) 20 and 40 cm depths at LFC and BdL; (ii) 30 and 60 cm depths at TCM; (iii) 40 cm depth and from the accumulation chamber (where only VOCs were analysed) at LL, the latter to assess the effective abatement of the discharge of VOCs from cover soil to the atmosphere. At TCM, soil gas sampling was extended further down due to the high fracturing of soil owed to ploughing activities, periodically taking place in the area, which enhanced air permeation in the first tens of centimetres. Before soil gas sampling, CO₂ and CH₄ soil flux measurements were carried out. Complete datasets of inorganic and organic compositions from the corresponding gas vents (e.g., fumaroles, bubbling pools, dry vents) and landfill gas were also reported for each study area, being representatives of the source gas composition.

3.2. Φ_{CO_2} and Φ_{CH_4}

The Φ_{CO_2} and Φ_{CH_4} values were measured using the “non-stationary static accumulation chamber” (AC) method with West Systems™ portable fluxmeters (Fig. 2a). An open-bottom cylindrical metallic

container (chamber) with a basal area of approximately 300 cm² and an inner height of about 10 cm was firmly placed on the ground. Gases escaping from the soil accumulated in the chamber volume that was continuously transferred by a low-flux pump (20 mL/s), after passing a water trap and a particulate filter, to the gas detectors consisting of an infrared sensor for CO₂ and a tuneable diode laser absorption spectroscopy for CH₄; then, the gas was re-injected into the chamber. The values of CO₂ and CH₄ concentrations were continuously recorded by a palmtop computer and displayed in a binary plot concentration vs time. The flux values (Φ) were computed by the slope of the straight line fitting the early increase of the gas concentration over time (dC/dt) inside the chamber and the proportionality factor k , according to the following equation (eq. 1; Cardellini et al., 2003; Chiodini et al., 1996, 1998):

$$\Phi = k \times \frac{dC}{dt} \quad (1)$$

The proportionality factor k was determined at the manufacturing company (West Systems™) before each sampling survey by means of laboratory tests. Overall, the obtained reproducibility was >5 % for $\Phi_{CO_2} > 44 \text{ g m}^{-2} \text{ d}^{-1}$ and $\Phi_{CH_4} > 16 \text{ g m}^{-2} \text{ d}^{-1}$ and about 10 % for lower flux values.

The “static accumulation closed-chamber” (CC) method (Fig. 2a) was preferred over the AC method to measure Φ_{CH_4} at Vulcano Island due to its better sensitivity and accuracy in the measurement of low soil CH₄ effluxes (Tassi et al., 2011). Operatively, the CC method is based on polypropylene open-bottom chambers (basal area = 177 cm² and inner volume = 4415 cm³), equipped with a sampling port on the top, placed on the ground. A series of gas samples (approximately 20 mL volume each) were taken from each positioned chamber at regular time intervals, i.e., just after the chamber was positioned (time 0) and after 5 and 10 min, by using a 60 mL luer-lock syringe. Gas samples were then transferred into 12 mL glass vials (Labco Exetainer®) (Fig. 2a). CH₄ concentrations were determined in the laboratory by using a gas chromatograph. The flux values were computed by the following equation (eq. 2; Tassi et al., 2011):

$$\Phi = \frac{V}{A} \times \frac{dC}{dt} \quad (2)$$

The dC/dt ratio represents the concentration increase over time as computed from the linear regression of the three concentrations detected within the chamber at the three sampling times. V and A are the volume and the basal area of the chamber, respectively.

The computed flux values were finally corrected with ambient temperature and air pressure recorded at each sampling site.

3.3. Sampling methods for gases

3.3.1. Gases from the non-stationary static accumulation chamber

Sampling campaigns at LL were carried out by using an AC chamber equipped, on its top, with a port, connected to a three-way valve, to allow the collection of gases accumulating within the chamber itself. At the end of each flux measurement, gases enclosed within the chamber were collected by connecting a 60 mL luer-lock syringe to the chamber's three-way valve and transferred into the 12 mL glass vial (Labco Exetainer®) (Fig. 2a).

3.3.2. Interstitial soil gases

Interstitial soil gases were collected from a 90 cm long stainless-steel probe (inner diameter = 4 mm) inserted within the soil down to the selected depths (Fig. 2b). The top of the probe was equipped with a silicon tube connected to a PTFE three-way valve. Soil gases were pulled out by using a 100 mL plastic syringe, connected through the PTFE three-way valve, and transferred into the 12 mL glass vial (Labco Exetainer®). Prior to the sampling, the air contained in the sampling line was flushed with soil gas.

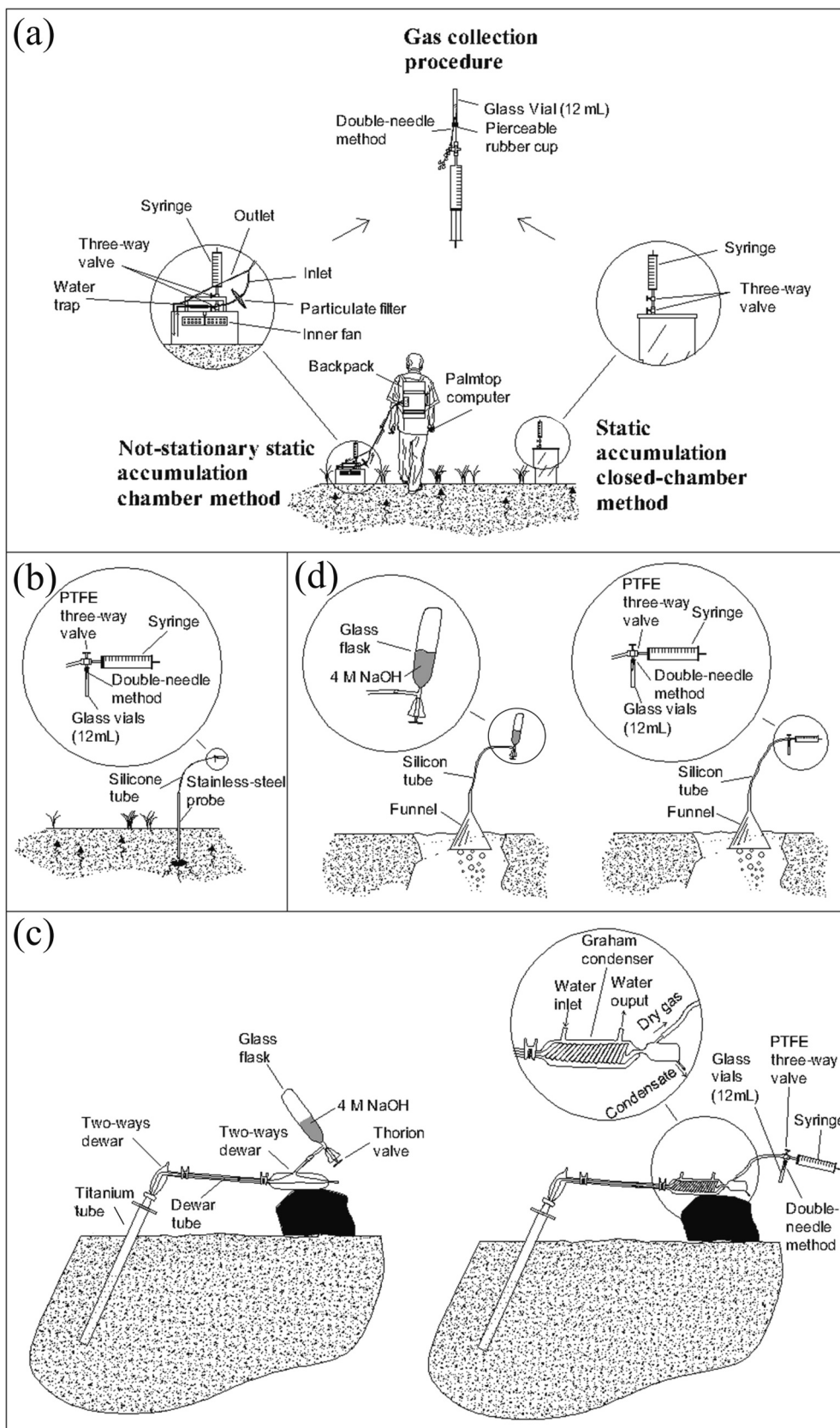


Fig. 2. Sketches of: (a) the apparatus for the measurement of gas fluxes by the non-stationary static accumulation chamber (AC) and static accumulation closed-chamber (CC) method, including the scheme of gas collection by using the double-needle method; (b) the procedure for interstitial soil gas collection, as described in the text (Section 3); the sampling of (c) fumarolic and (d) bubbling main (on the left) and C_{4+} organic (on the right) gas components as reported in the text (Section 3).

3.3.3. Fumarolic gases

Gases from the fumarolic fluid from LFC were sampled following the method reported by Vaselli et al. (2006) (Fig. 2c). A 70 cm long titanium tube was inserted into the fumarolic conduit and gases were conveyed into the storage vessel through a dewar glass tube line. On the basis of the analytes to determine, two different sampling techniques were adopted. For the determination of the main gas components (CO_2 , acidic species, H_2 , O_2 , N_2), the titanium tube was connected, through dewar glass tubes jointed by ball-and-socket-type joints, to a sampling flask consisting of a pre-weighted and pre-evacuated glass bottle (60 cc) equipped with a Thorion® valve and partially filled with ~20 mL of a 4 M NaOH solution to entrap acidic species and to enrich the headspace volume with the non-condensable gases (H_2 , N_2 , O_2 , CH_4 and Ar). For the analysis of C_4+ organic gas constituents, as an interaction of these gas species with the alkaline solution was expected (Vaselli et al., 2006), an aliquot of volcanic fluids was collected after removing the steam and the acidic gases by using a Graham condenser cooled by water and placed along the sampling glass line. The dry gas fraction was collected from the headspace of the condenser by using a 100 mL conical syringe and transferred into pre-evacuated 12 mL glass vials (Labco Exetainer®).

3.3.4. Bubbling gases

Bubbling gases from BdL were collected by using a funnel, upside-down positioned above the gas bubbles (Fig. 2d). The funnel was connected through a silicon tube to (i) a pre-evacuated glass flask partially filled with ~20 mL of a 4 M NaOH solution volume for the analysis of the main components (CO_2 , acidic species, H_2 , N_2 , O_2 , CH_4 and Ar), and (ii) to 12 mL glass vials (Labco Exetainer®) for the analysis of the C_4+ organic gas constituents.

3.3.5. Landfill gases

The landfill gas sample was collected from the main manifold that comprised pipes for receiving landfill gas recovered by deep wells. Gases were stored into a 12 mL glass vial (Labco Exetainer®) connecting to the port of the pipe a simple sampling line consisting of (i) silicon tubes, (ii) a three-way valve, and (iii) a 60 mL luer-lock syringe.

3.4. Analytical methods

The main gas components in the glass vials (CO_2 , CH_4 , N_2 , O_2 , and Ar) and the inorganic gases (N_2 , O_2 , H_2 , and Ar) in the glass flasks were measured by gas-chromatography (GC) using a Shimadzu 15 A gas chromatograph with a 9 m long 5 A molecular sieve column and a thermal conductivity detector (TCD). CO_2 and the other acidic gases (here reported as a sum) dissolved in the alkaline solution of the glass flasks were analysed as anions by automatic titration with 0.5 M HCl solution (Metrohm 794 Basic Titrino) and ion-chromatography (Metrohm 761 Compact IC). Light hydrocarbons (C_1 – C_4), except CH_4 at high concentrations (> 0.5 % by vol), were analysed by GC using a Shimadzu 14 A gas chromatograph supplied with a hydrogen flame ionisation detector (FID) and a 10 m long stainless-steel column ($\Phi = 2$ mm) packed with Chromosorb PAW80/100 mesh coated with 23 % SP 1700. Both GCs worked using He as a carrier gas. The analytical errors for both GC-TCD and GC-FID were < 5 %.

The identification and quantification of C_4+ VOCs were performed by employing the solid phase microextraction method (Arthur and Pawliszyn, 1990) and a Thermo Trace Ultra GC coupled with a Thermo DSQ Quadrupole mass spectrometer. A 2 cm long three-phase fibre composed of divinylbenzene and carboxen - polydimethylsiloxane mixture (Supelco) was inserted into the glass vials through the pierceable rubber cap and exposed to the gas samples for 30 min at ambient temperature (20 °C). C_4+ VOCs extracted from the gas samples and retained on the fibre were desorbed in the headspace of the GC column for 2 min at 230 °C and introduced into a 30 m \times 0.25 mm (inner diameter = 0.25 μm) film thickness TR-V1 fused silica capillary column (Thermo), using

He as a carrier gas. Analytes separated by the chromatographic column were conducted to the quadrupole mass spectrometer (set in full-scan mode, i.e., operating in the 40–400 m/z mass range) through a transfer-line set at 230 °C. The mass detector worked in a positive electron impact (EI) mode. The ionisation energy and the source temperature were set at 70 eV and 250 °C, respectively. C_4+ VOCs were identified on the basis of the retention times of the chromatographic peaks and the comparison of the resulting mass spectra with those provided by the database of the NIST05 library (NIST, 2005). Quantitative analysis implied the use of a proper external standard calibration procedure. This was based on calibration curves constructed by measuring Accustandard® standard liquid mixtures in methanol or, alternatively, hexane solvents at increasing concentrations as described by Tassi et al. (2012a). The relative standard deviation computed by five replicate analyses of the standard mixture was <5 %. The limit of quantification (LOQ) corresponded to the area of a peak having a signal/noise ratio of 5. LOQ was extrapolated in agreement with the lowest concentration of the standard mixtures used for the calibration curve.

3.5. Datasets from previous works

Published geochemical data from 3 different medium enthalpy hydrothermal systems was considered in this study, as follows: (i) Solfatara di Nepi (NP) and (ii) Caldara di Manziana (MZ), including 99 and 96 soil gas samples collected at 20 and 40 cm depth, respectively, ΦCO_2 and ΦCH_4 measurements, and the chemical compositions of a gas vent (NPgas) and a bubbling pool (MZgas) (Venturi et al., 2024); (iii) Poggio dell'Ulivo (PdU), consisting of the chemical composition of 25 and 5 soil gas samples collected at 40 and 20 cm depth, respectively, and a bubbling pool (PdUgas) (Tassi et al., 2015b). The high enthalpy hydrothermal system of the Solfatara crater (SF) was also included in the study. SF dataset consisted of the analytical data of 52 soil gas samples collected at 30 cm depth and a fumarole (SFgas; being computed by averaging the compositions of the two main fumarolic discharges of SF, i.e., BG and BN; Tassi et al., 2015a), and ΦCO_2 and ΦCH_4 measurements.

4. Results

4.1. Vulcano Island

4.1.1. Inorganic and organic compositions of fumarolic and bubbling gas

Fumarolic (LFCgas) and bubbling (BdLgas) gases were collected from selected vents located at the northern flank of the LFC and close to the shoreline, respectively (Fig. 1a, b). The dry composition of LFCgas was dominated by CO_2 (94 % by vol) and acidic gases (4.8 % by vol), followed by N_2 (1.7 % by vol), H_2 (0.02 % by vol), CH_4 , (9×10^{-4} % by vol), Ar (8×10^{-4} % by vol) and O_2 (3×10^{-4} % by vol; Table S.1). BdLgas, dominated by CO_2 (98.6 % by vol), was relatively enriched in CH_4 (0.17 % by vol) and H_2 (0.24 % by vol), whilst acidic gases (0.89 % by vol), N_2 (0.28 % by vol), Ar (2×10^{-3} % by vol) and O_2 (3×10^{-4} % by vol) occurred at relatively low amounts (Table S.1).

A total of 19 different VOCs were identified in both LFCgas and BdLgas, accounting for a total of 14 and 398 ppbv, respectively. Overall, alkane and S-substituted compounds were the most abundant organic groups in LFCgas accounting for 49 and 21 % of total VOC composition (ΣVOCs), respectively. Aromatic and alkene compounds were found in significant concentrations in LFCgas (13 and 11 % ΣVOCs , respectively), whilst the contents of halogenated, furan, phenol and aliphatic O-substituted (i.e., only aldehydes) compounds were relatively low (2.6, 1.5, 0.7 and 0.7 % ΣVOCs , respectively). Alkanes, by far dominating the organic composition of BdLgas (70 % ΣVOCs), were followed by aromatic and alkene compounds (16 and 11 % ΣVOCs , respectively), whilst S-substituted, halogenated, furan, phenol and aliphatic O-substituted (i.e., only aldehydes) compounds constituted the lowest fractions (1.9, 0.6, 0.08, 0.05 and 0.03 % ΣVOCs , respectively).

4.1.2. ΦCO_2 and ΦCH_4 values and inorganic and organic compositions of soil gases

Soil gas sampling and soil flux measurements of CO_2 (AC method) and CH_4 (CC method) were performed in 45 selected sampling sites located as follows: (i) 24 in LFC and (ii) 21 in BdL, of which 10 were next to the beach and 11 in the tuff cone area nearby the harbour (Fig. 1a, b). A total of 78 interstitial soil gas samples were collected at 20 and 40 cm depths; the soil in 13 sampling sites was too compacted to permit the insertion of the sampling probe down to 40 cm depth.

The measured ΦCO_2 values were generally lower in LFC (ranging from 4.6 to 2260 $\text{g m}^{-2} \text{day}^{-1}$; Fig. S.1a) with respect to those detected in BdL (ranging from 36.4 to 4140 $\text{g m}^{-2} \text{day}^{-1}$; Fig. S.1b). Similarly, the ΦCH_4 values in LFC (ranging from 2×10^{-4} to 0.03 $\text{g m}^{-2} \text{day}^{-1}$; Fig. S.1a) were overall lower than those in BdL (ranging from 4.4×10^{-4} to 0.19 $\text{g m}^{-2} \text{day}^{-1}$; Fig. S.1b). The highest ΦCH_4 values were found in the correspondence of the highest ΦCO_2 values, whilst CH_4 fluxes were virtually undetectable in sampling sites experiencing the lowest ΦCO_2 values.

The chemical composition of interstitial soil gas samples from both LFC and BdL spanned from N_2 -dominated to CO_2 -dominated. Most gases collected at 20 cm depth were enriched in N_2 (ranging from 2.01 to 77.1 % by vol; Fig. S.2a, b) with respect to the corresponding deeper gases (ranging from 2.77 to 75.4 % by vol; Fig. S.2a, b). An opposite trend was shown by CO_2 whose levels generally increased downwards along vertical profiles (i.e., from 5.92 to 97.9 % by vol at 20 cm depth to 7.62–97.0 % by vol at 40 cm depth; Fig. S.2a, b). The amounts of O_2 and Ar, overall ranging from 0.03 to 19.8 % and from 0.02 to 0.89 % by vol (Fig. S.2a, b), were linearly correlated to the N_2 contents. The contents of CH_4 , which represented the least abundant component among those measured in soil gas samples, were positively correlated to the contents of CO_2 and were higher (about one order of magnitude) in BdL soil gases (ranging from 4.4×10^{-3} to 0.08 % by vol, at 40 cm depth, and from 5×10^{-6} to 0.07 % at 20 cm depth; Fig. S.2b) with respect to the soil gases collected from LFC (ranging from 3.5×10^{-4} to 7.8×10^{-3} % by vol, at 40 cm depth, and from 5.0×10^{-6} to 5.6×10^{-3} % by vol at 20 cm depth; Fig. S.2a).

Up to 37 and 54 different VOCs were detected in soil gas samples from LFC and BdL. Overall, the LFC soil gas samples showed lower contents of VOCs (ranging, as a sum, from 1.1 to 264 ppbv; Fig. S.3a) compared to those from BdL (ranging, as a sum, from 1.5 to 1370 ppbv; Fig. S.3b).

The VOC composition in the soil gases from LFC varied largely among the different sampling sites compared to the soil gases collected from BdL. Overall, the VOC composition of soil gases from LFC and BdL were dominated by alkanes that ranged, with variable trends with depth, from 36 to 76 % and from 36 to 86 % ΣVOCs at 20 cm and 40 cm depth, respectively (Fig. S.4a). Aromatic, S-substituted, aliphatic O-substituted (including aldehydes, esters and ketones) and furan compounds were detected in relatively lower amounts, i.e., up to 45 %, 33 %, 14.5 %, and 24.5 % ΣVOCs , respectively (Fig. S.4a). Overall, soil gases from BdL exhibited relatively low levels of S-substituted, aliphatic O-substituted and furan compounds with respect to those from LFC (Fig. S.4b). Halogenated, cyclic, alkenes and phenol compounds, except in rare cases, occurred in subordinate relative contents with respect to the other organic groups in all soil gas samples, accounting for <6.8 %, < 11 %, < 2.1 % and < 1.8 % ΣVOCs , respectively (Fig. S.4a, b). Soil gases collected at 20 cm depth were relatively enriched in aliphatic O-substituted, furan and halogenated compounds and depleted in S-substituted and alkenes compounds compared to deeper gases along the corresponding vertical profiles (Fig. S.4a, b).

4.2. Terre Calde di Medolla

4.2.1. Inorganic and organic compositions of deep gas

Since no punctual vent exhaled in TCM, the gas sample (TCMgas) collected at 90 cm depth from the site exhibiting the highest ΦCO_2 and

ΦCH_4 values (170.0 and 34.40 $\text{g m}^{-2} \text{day}^{-1}$, respectively; Table S.2) was adopted as the best representative of the deep gas composition (Fig. 1c).

TCMgas was by far dominated by CH_4 (97.1 % by vol), followed by N_2 (2.34 % by vol), CO_2 (0.43 % by vol), O_2 (0.11 % by vol) and Ar (0.03 % by vol) (Table S.2). A total of 42 different VOCs were identified, constituting as a sum about 1,180,000 ppbv of the total gas composition. Alkanes represented the most abundant organic group followed by cyclics and alkenes, accounting for 94, 5.6 and 0.9 % ΣVOCs , respectively. Aromatic, aliphatic O-substituted (including aldehydes, esters, ketones and alcohol), phenol, halogenated and terpene compounds occurred at minor amounts, representing 7×10^{-3} , 1×10^{-3} , 1×10^{-3} , 8×10^{-4} and 6×10^{-5} % ΣVOCs , respectively.

4.2.2. ΦCO_2 and ΦCH_4 values and inorganic and organic compositions of soil gases

The ΦCO_2 and ΦCH_4 measurements (AC method) and soil gas sampling at 30 and 60 cm depths were carried out in 5 sampling sites within a subcircular CH_4 -dominated macroseepage, which was noticeable from the relatively high ΦCH_4 and the occurrence of senescent vegetation (Fig. 1c). The ΦCO_2 and ΦCH_4 values ranged from 14.8 to 28.8 $\text{g m}^{-2} \text{d}^{-1}$ and from 16.3 to 52.7 $\text{g m}^{-2} \text{d}^{-1}$ (Fig. S.1c).

Soil gas samples collected at 30 and 60 cm depths were characterised by relatively high CH_4 concentrations (ranging from 19.3 to 87.8 % by vol and from 36.7 to 88.5 % by vol, respectively), which decreased upwards along vertical profiles, followed by N_2 (ranging from 11.0 to 63.7 % by vol and from 8.90 to 50.7 % by vol, respectively), CO_2 (ranging from 0.25 to 12.36 % by vol and from 0.13 to 10.8 % by vol, respectively), O_2 (ranging from 0.82 to 3.59 % by vol and from 0.52 to 1.15 % by vol, respectively) and Ar (ranging from 0.14 to 0.79 % by vol and from 0.11 to 0.63 % by vol, respectively) (Fig. S.2c).

A total of 44 different VOC species were identified in soil gases. The TCM soil gas samples at 30 and 60 cm depths contained large amounts, as a sum, of VOCs that ranged from 228,000 to 871,000 ppbv (Fig. S.3c). The organic composition of soil gases was rather coherent with that seen for TCMgas: alkanes were by far the most abundant organic group accounting for 89 to 96 % ΣVOCs , with higher values on average at deeper depths, followed by cyclic and alkene compounds (ranging from 3.7 to 10 % and from 0.44 to 0.95 % ΣVOCs , respectively) with no clear trend with depth. Aliphatic O-substituted (variable proportion of aldehydes, esters, ketones and alcohols) and terpene compounds ranged from 6×10^{-3} to 0.04 % and from 1×10^{-4} to 1×10^{-3} % ΣVOCs , respectively, with higher contents found at the shallow depth (Fig. S.4c). Aromatics, halogenated compounds and phenol were found in trace amounts (ranging from 4×10^{-3} to 0.01 %, from 5×10^{-4} to 2×10^{-3} % and from 3×10^{-3} to 0.01 % ΣVOCs , respectively), varying with no clear trend with depth (Fig. S.4c).

4.3. Legoli landfill

4.3.1. Inorganic and organic compositions of landfill gas

The chemical composition of the landfill gas sample (i.e., LLgas) was dominated by CH_4 (52.4 % by vol), followed by CO_2 (32.0 % by vol, respectively), N_2 (13.3 % by vol, respectively), O_2 (2.12 % by vol, respectively) and Ar (0.16 % by vol, respectively) (Table S.3).

A total of 53 different VOC species, accounting, as a sum, for 1,120,000 ppbv were detected. The organic composition was largely dominated by aromatic and alkane followed by cyclic, halogenated and terpene compounds that accounted for 58, 18, 12, 11 and 0.4 % ΣVOCs , whilst the relative amounts of S-substituted, aliphatic O-substituted (including aldehydes, esters, ketones and alcohols), phenol and N-substituted compounds were lower than 0.2 % ΣVOCs .

4.3.2. ΦCO_2 and ΦCH_4 values and inorganic and organic compositions of soil gases

A total of 69 sampling sites (i.e., 38 within L1, 20 within L2 and 11 pertaining to L3) were arrayed at interval distances ranging from 35 to

80 m (Fig. 1d). At each sampling site, both ΦCO_2 and ΦCH_4 fluxes were measured by using the AC method and gas samples were collected (i) from the accumulation chamber just after the flux measurements for VOC analyses and (ii) at 40 cm soil depth. Given the extremely low permeability of the soil that hindered gas withdrawal, no soil gas sample was collected in 19 sites.

Overall, ΦCO_2 and ΦCH_4 values ranged in wide intervals, i.e., from 1.00 to 209 $\text{g m}^{-2} \text{day}^{-1}$ and from 0.06 to 111 $\text{g m}^{-2} \text{day}^{-1}$, respectively, with the sole exception of the LL #58 and #68 sampling sites where the values of ΦCO_2 and ΦCH_4 were > 917 and > 369 $\text{g m}^{-2} \text{day}^{-1}$, respectively (Fig. S.1d).

Interstitial soil gas samples collected at 40 cm depth were characterised by high contents of N_2 (ranging from 29.9 to 93.9 % by vol), directly correlated to the concentrations of O_2 (ranging from 0.21 to 16.1 % by vol) and Ar (ranging from 0.33 to 1.12 % by vol; Fig. S.2d). The concentrations of CO_2 and CH_4 , positively correlated to each other, varied in relatively large ranges, i.e., from 0.02 to 33.0 % and from 2.1×10^{-3} to 36.5 % by vol (Fig. S.2d).

Up to 54 and 39 different VOC species were identified in the gases from the soil and from the accumulation chamber, respectively. In the interstitial soil gas samples, VOCs constituted from 129 to 1,410,000 ppbv, whilst the concentrations in the corresponding gases collected from the accumulation chamber were proportionally lower (ranging from 73 to 122,000 ppbv) (Fig. S.3d). The VOC compositions of soil gases were reciprocally dominated by either aromatics and alkanes (ranging from 15 to 69 % and from 12 to 37 % ΣVOCs , respectively) or by the aliphatic O-substituted (mainly esters with variable proportions

of aldehydes and ketones and minor amounts of alcohols) and terpene compounds whose relative abundances reached 34 % and 33 % ΣVOCs , respectively (Fig. S.4d). Cyclic and halogenated compounds occurred in relatively significant amounts (accounting for up to 12 and 25 % ΣVOCs , respectively), whilst S-substituted, phenol and N-substituted compounds overall occurred in minor relative amounts, i.e., < 2.7 , < 0.5 and < 0.01 % ΣVOCs , respectively (Fig. S.4d). Compared to the corresponding soil gas compositions, the organic composition of gases collected within the accumulation chamber was enriched in aliphatic O-substituted (including variable amounts of aldehydes, esters and ketones with no alcohols) and terpene compounds that, in most cases, were the most abundant organic groups, spanning from 4×10^{-3} to 87 % and from 0.27 to 43 % ΣVOCs , respectively (Fig. S.4d). On the other hand, the contents of aromatics and alkanes in these gases varied over ranges of 5.6–84 % and 0.82–22 % ΣVOCs , respectively (Fig. S.4d). Cyclic, halogenated compounds and S-substituted compounds were sporadically detected, and their contents did not exceed 7.9, 17 and 0.86 % ΣVOCs , respectively, whilst no phenol nor N-substituted compounds appeared (Fig. S.4d).

5. Discussion

5.1. Origin and composition of hypogenic VOCs

The sum of VOC concentrations (ΣVOCs) in fluids from the hypogenic gas sources (LFCgas, BdLgas, TCMgas, MZgas, NPGas, PdUgas, SFgas, and LLgas) increased at decreasing temperatures of the associated

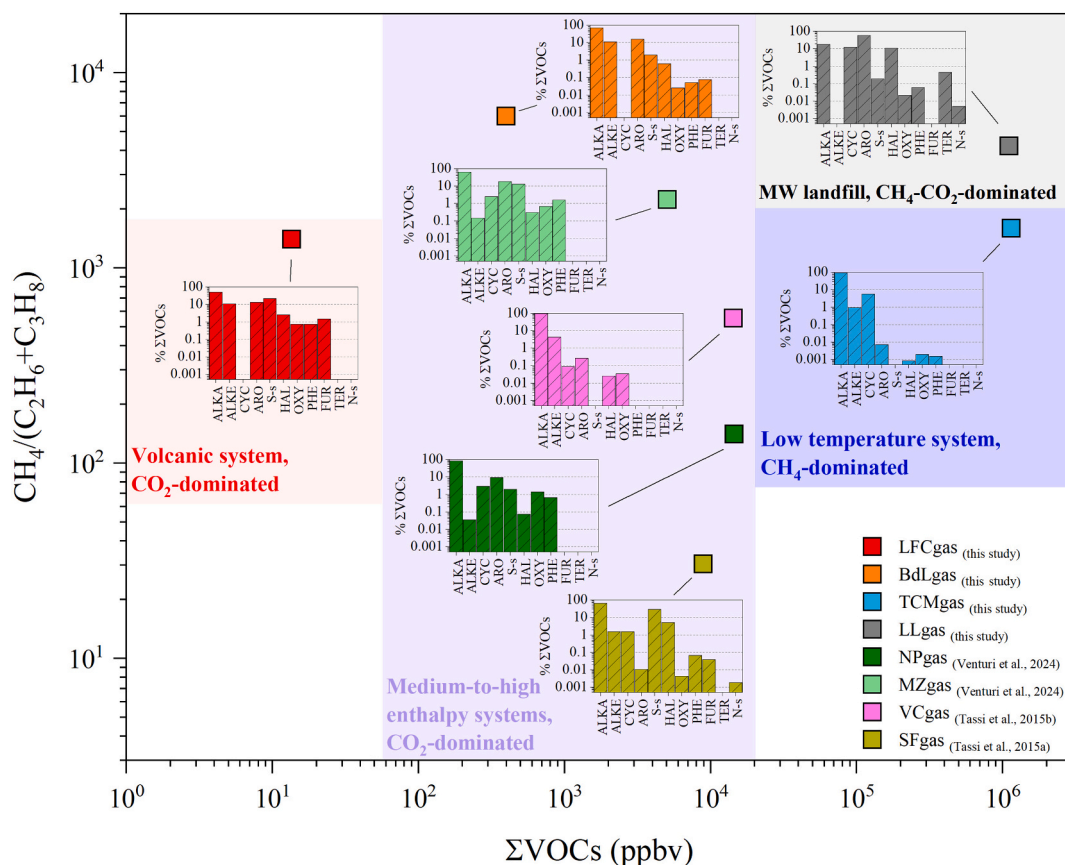


Fig. 3. $\text{CH}_4/(\text{C}_2\text{H}_6 + \text{C}_3\text{H}_8)$ ratios vs total concentration of VOCs (expressed as ppbv) of gas vents and landfill gas collected from (i) La Fossa crater, Baia di Levante, Terre Calde di Medolla and Legoli landfill (LFCgas, BdLgas, TCMgas and LLgas, respectively; this study); (ii) Solfatara di Nepi and Caldara di Manziana (NPGas and MZgas, respectively; Venturi et al., 2024); (iii) Poggio dell'Ulivo (PdUgas; Tassi et al., 2015b); (iv) Solfatara crater (SFgas; Tassi et al., 2015a). Bar charts of organic functional group concentrations, as a sum, of VOCs (expressed as % ΣVOCs) are also reported. Legend: ALKA = alkanes; ALKE = alkenes; CYC = cyclics; ARO = aromatics; S-s = S-substituted compounds; HAL = halogenated compounds; OXY = aliphatic O-substituted compounds (including aldehydes, esters, ketones, alcohols and organic acids); PHE = phenol; FUR = furans; TER = terpenes; N-s = N-substituted compound, i.e., benzothiazole.

system, i.e., from volcanic systems (LFC; Costa et al., 2020) to CH₄-dominated fluids (TCM; Sciarra et al., 2017) and the landfill (LL; Fig. 3), with intermediate values shown by medium-to-high enthalpy systems, including BdL, NP, MZ, PdU and SF (up to 360 °C; Capaccioni et al., 2001; Cinti et al., 2018; Tassi et al., 2015a, 2015b). The paucity of VOCs in the CO₂-dominated gases originating at hydrothermal and, especially, volcanic conditions was not surprising, since VOCs are rapidly degraded by chemical reactions at increasing temperatures (Capaccioni et al., 1995; Linton and Turnbull, 1984). On the other hand, VOCs in the CH₄(CO₂)-dominated gases were favoured by the relatively low temperatures and the abundance of organic matter typical of the natural (TCM) and anthropogenic (LL) environments associated with these fluids (Mattavelli and Novelli, 1988; Ricci et al., 2023; Chu et al., 2021; Sciarra et al., 2021).

As reported in the literature (e.g. Tassi et al., 2012d and references therein), microbial degradation of organic matter tends to produce gases characterised by relatively high CH₄/(C₂H₆ + C₃H₈) ratios (> 1000), whilst lower values (<100) are commonly ascribed to thermogenic gases since thermogenesis is less selective in generating light-molecular weight alkanes. While these intervals crystallised the biogenic origin of VOCs for TCMgas and LLgas, they appeared misleading for gas vents from the medium-to-high enthalpy systems (Fig. 3): only SFgas fell strictly within the thermogenic range. The apparent shift of gases from medium-to-high enthalpy systems to the microbial-sourced field from the pertaining thermogenic interval was likely caused by secondary processes during the gas upwelling and/or transformations of molecules in the gas reservoir rather than high contributions of microbially driven degradation of organic matter, being it severely compromised at the temperatures expected in their origin reservoirs (> 100 °C) (Rice and Claypool, 1981). These processes could include: (i) molecular fractionation (Milkov and Etiope, 2018); (ii) CH₄ production by CO₂ reduction (Chiodini, 2009; Tassi et al., 2012b); (iii) dehydrogenation of light alkanes, favoured at high temperature and oxidising conditions typical of volcanic environments (Tassi et al., 2012c).

Relevant similarities and interesting differences were observed among the chemical composition of VOCs in the geogenic gases from different sites, indicating the action of local site-specific constraints (Fig. 3). The composition of VOCs in all geogenic gases was dominated by alkanes (Fig. 3), consistently with other natural gaseous exhalations worldwide (e.g., Tassi et al., 2012a, 2012c, 2010; Whelan and Hunt, 1983). The alkane series invariably exhibited a general decreasing trend of concentrations with increasing carbon numbers (Tables S.1 and S.2; Tassi et al., 2015a, 2015b; Venturi et al., 2024). This evidence implied either a preferential generation or a relatively high stability of short saturated acyclic compounds regardless of the enthalpy of the geogenic environment of formation. In fact, thermodynamic computations indicate that the heavier is the molecular weight of alkanes the higher is the free energy of formation per carbon atom at any temperature (Capaccioni et al., 1995). Moreover, the alteration of buried organic matter in hydrothermal systems can selectively extract short-chain alkanes depending on temperature and pressure (Petrov et al., 2021). At relatively high temperatures, such as those typical of active volcanoes, abiotic carbon compound polymerisation (Fischer-Tropsch synthesis), which generates an organic compound suite mainly consisting of CH₄ and short-chain n-alkanes, was also invoked (McCullom and Seewald, 2007).

Light alkenes were found in significant concentrations in all volcanic and hydrothermal geogenic gases (Fig. 3), where the formation of C₃-C₅ alkenes is commonly attributed to alkane dehydrogenation reactions (Capaccioni and Mangani, 2001; Seewald, 2001; Tassi et al., 2012c). Differently, the C₆-C₈ alkenes, the only alkenes recognised in TCMgas (Table S.2), may have been produced by the decomposition of buried organic matter at relatively low temperatures (Mahlstedt, 2020), since alkane dehydrogenation is not efficient at temperatures <150 °C (Gomez et al., 2019; Mango et al., 1994).

Cyclic compounds in volcanic/hydrothermal gases (LFCgas and

BdLgas) did not occur or were found in low concentrations (Fig. 3), in agreement with previous findings (Tassi et al., 2010), whilst these VOCs are generally enriched in oil and biogenic gases (Guzmán et al., 2022; Hu et al., 2010; Polyakov and Horita, 2021). In volcanic-hydrothermal fluids, i.e., at relatively high temperatures and oxidising conditions, the catalytic dehydrogenation and aromatisation of cyclics are favoured (Konn et al., 2015; Tassi et al., 2012a; Venturi et al., 2017), whilst this process is not efficient in gases from systems at decreasing enthalpy (MZgas, NPgas, PdUgas, SFgas, and TCMgas) that showed, consequently, increasing concentrations of cyclics (Fig. 3).

Aromatics were detected in significant amounts in the volcanic and hydrothermal exhalations, whilst they were found in subordinate amounts in TCMgas (Fig. 3). Many processes have been invoked to explain their origin in geogenic fluids: (i) degradation of sugars under hydrothermal conditions (Konn et al., 2015); (ii) abiotic clay-catalysed synthesis (McCullom, 2013); (iii) catalytic aromatisation of CH₄ (Taran and Giggenbach, 2003); (iv) catalytic dehydrogenation of cycloalkanes (Venturi et al., 2017). These processes are favoured by (i) medium-to-high temperatures and (ii) chemical catalysts (e.g., sulfur gases, Al-silicates, iron oxides and sulphide minerals; Capaccioni et al., 2004, 1995; Tassi et al., 2010), both conditions being typical of volcanic-hydrothermal systems. The relatively low concentration of aromatic compounds in TCMgas (Fig. 3) may be interpreted as related to the low temperature characterising this environment, i.e., too low to complete the aromatisation of cycloalkanes and cycloalkenes (Behar et al., 1992; Hu et al., 2014; Venturi et al., 2017). Low temperature conditions characterising the TCM source likely hindered the thermal demethylation of branched aromatics, explaining the dominance of toluene over benzene compared to the medium-to-high temperature gas vents (Table S.1, S.2; Tassi et al., 2015a, 2015b; Venturi et al., 2024).

The significant contents of S-substituted compounds marking the volcanic and hydrothermal fluids (Fig. 3) may reasonably be related to the high fugacity of sulfur due to S-bearing gases from magmatic degassing and volcanic gas-water-rock interactions (Sánchez-Avila et al., 2021; Schwandner et al., 2013; Tassi et al., 2010). Accordingly, the lack of S-substituted compounds in PdUgas and TCMgas (Fig. 3) reflected the low availability of reacting sulfur volatile species in these systems (Tassi et al., 2015b; Table S.2), although organosulfur compounds in a sedimentary domain mainly originate from (i) degradation of sulfur-contained organic matter, (ii) metabolic activity of sulfur-reducing bacteria, and (iii) thermochemical sulfate reduction mechanisms at temperatures >100–140 °C (Amrani, 2014; Machel, 2001; Shi and Wu, 2021).

The occurrence of halocarbons in the geogenic gas samples of this study (Fig. 3) may have been ascribed, to a variable extent, to (i) the availability of halides in the reservoir and the proceeding degrees of halogenation processes (Aarnes et al., 2011; Jordan et al., 2000; Keppler et al., 2000; Schreiber et al., 2017; Svensen et al., 2009) and (ii) air contamination (Frische et al., 2006). However, bio-halogenated compounds in deep natural systems could not be ruled out (Silk et al., 1997; Zhang et al., 2021).

Aliphatic O-substituted compounds pertaining to ketone, ester, aldehyde, alcohol and organic acid groups were found in relatively low contents in the investigated geogenic gases (Fig. 3), in agreement with the composition of VOCs in gases from hydrothermal and volcanic systems worldwide and sedimentary basins (Isidorov et al., 1990; Bonini et al., 2013; Tassi et al., 2010, 2009a, 2012c), and clearly related to the reducing conditions characterising the geogenic fluid source. Such limited amounts of aliphatic O-substituted compounds may have been generated by hydration and subsequent oxidation of alkanes at hydrothermal conditions (Seewald, 2001; Yang et al., 2012) and by diagenesis and pyrolysis of organic matter (Leif and Simoneit, 1995, 2000; Sandison et al., 2003; Volkman et al., 2000). Bio-oxidation of geogenic non-oxygenated VOCs (e.g., alkanes, aromatics, thiophenes, alkenes, cyclics) at both surficial and sub-surficial environments, where O₂ supply is not limited, likely acted as an additional source of esters,

ketones, aldehydes, organic acids and phenol in geogenic fluids (Kokh et al., 2017; Sánchez-Avila et al., 2021; Tassi et al., 2013b). The last O-bearing compound exhibits a peculiar behaviour with respect to aliphatic O-substituted compounds due to the presence of an aromatic ring. Indeed, it is commonly found in hydrothermal/volcanic gases (Schwandner et al., 2013; Shock et al., 2013; Tassi et al., 2009a) and in fluids originating from the maturation of organic-rich source deposits (Dieckmann et al., 2006; Taylor et al., 1997; Fig. 3). Experimental evidence has demonstrated the hydrothermal formation of phenol as an intermediate product of decarboxylation of toluene (McCullom et al., 2001) and as a final product of the reaction of sodium hydrogen carbonate with water in the presence of iron powder (Tian et al., 2007).

Furans were detected only in gas vents from LFC, BdL and SF (Fig. 3). They are typical high-temperature aromatic O-bearing compounds and are supposed to be formed through the Paal-Knorr synthesis that involves the closure of oxygenated alkanes under highly acidic and oxidising conditions (Tassi et al., 2010, 2012c).

No terpenes were found in the investigated geogenic gases, except α -pinene in the TCMgas (Fig. 3; Table S.1) that is the main constituent of the VOC suite of living plant mechanisms (Mofikoya et al., 2020; Tripathi and Sahu, 2020). Terpenes are mainly synthesised by plants' metabolisms (Calogirou et al., 1999; Gershenson and Dudareva, 2007; Silvestre and Gandini, 2008) as well as degradation of vegetative parts of plants typically releases terpenes (Randazzo et al., 2022) and when found in deep-sourced gases, they are generally ascribed to litter decomposition at shallow depths (Isidorov et al., 1990; Schwandner et al., 2004).

A special mention was deserved to benzothiazole, an aromatic compound with S and N as substituents, which was found in SFgas (Fig. 3) likely due to anthropic pollution (Franklin et al., 2021). In fact, this compound is usually marked as a human-synthesised chemical, finding application in pharmaceutical and manufacturing industries (De Wever et al., 2001; Irfan et al., 2020), whereas its biogenic origin has not been demonstrated so far.

Compared to geogenic gases, the compositional features of VOCs in LLgas were marked by a significant fraction of aromatics, halogenated and terpene compounds as well as benzothiazole (Fig. 3). This pattern reflected a significant contribution of xenobiotic compounds and products from fresh organic matter degradation: VOCs from synthetic products commonly disposed of in municipal waste landfill (e.g., insecticides, solvents, paints, dyes, herbicides fungicides, air fresheners, pharmaceutical and antibacterial products, hydraulic and heat-transfer fluids) are dominated by these species, including alkanes (Bhatt et al., 2007; Gallego et al., 2014; Muennee et al., 2016; Pan et al., 2023; Randazzo et al., 2020). Moreover, degradation of the organic fraction of municipal waste (e.g., yard trimmings, food waste) releases significant contents of alkane, aromatic, cyclic, aliphatic O- and S-substituted compounds as well as phenol, but in different proportions with respect to those typically found in geogenic gases (Randazzo et al., 2022, 2023). Alkenes, which can be emitted by the degradation of the multi-component waste commonly disposed of in municipal waste landfills (Randazzo et al., 2022), were surprisingly not detected in LLgas (Fig. 3), presumably due to the reactivity of these compounds under aerobic conditions that can be established by the circulation of air and meteoric water within the landfill body.

5.2. Soil degradation processes affecting hypogenic gases

In the framework of this study, we referred to the soil as the surficial earthy layer, consisting of solid (organic and mineral matters), liquid and gaseous phases, interacting with the atmosphere, hydrosphere and biosphere. Bio-physicochemical conditions in soil dramatically differ from those characterising hypogenic gas reservoirs. For instance, air permeation and water infiltration boost oxidising conditions (Tassi et al., 2009b) and favour autotrophic and heterotrophic respiration (Kuzuyakov, 2006) through the promotion of different types of O₂

utilising microorganisms (Jabłońska and Tawfik, 2019), including methanotrophs and VOCs-degrading bacteria.

5.2.1. Main hypogenic gases (CO₂ and CH₄) in soil vs Φ CO₂ and Φ CH₄

All soil gases, except for most LFC and some of SF, exhibited noticeable depletions of CH₄ and to a lesser extent of CO₂, compared to those expected from the theoretical mixing between air and the hypogenic gas endmembers (Fig. 4). Methane depletion could reflect both CO₂ production by soil respiration (Le Mer and Roger, 2001) and CH₄ oxidation by methanotrophic bacteria (Fig. 4; Hanson and Hanson, 1996; Wang et al., 2023). The relative CH₄ enrichment with respect to their deep sources of most LFC and some SF soil gases (Fig. 4) was unlikely caused by CH₄ production through the anaerobic mineralisation of buried organic matter by strictly anaerobic bacteria at relatively shallow depths (Reay et al., 2018; Yang and Chang, 1998). Presumably, the LFCgas and SFgas composition may not exhaustively represent the deep gas source of the correspondent soil gases, as CH₄ concentrations may have shown significant variations in different discharging points of the same degassing system, depending on the consumption of this labile compound at relatively high temperatures such as those of the LFC and SF systems (Caliro et al., 2007; Chiodini, 2009; Tassi et al., 2012a).

Although it is commonly accepted that high Φ (CO₂ + CH₄) values counteract soil air permeation and limit gas-microbe and gas-soil interactions (Capaccioni et al., 2015; Randazzo et al., 2020; Venturi et al., 2019), with the sole exception of SF, CO₂ and CH₄ concentrations in soils were not (or only roughly) dependent on the extent of (CO₂ + CH₄) fluxes (Fig. 4). It suggested that spatial inhomogeneities in the physicochemical soil characteristics, local permeability barriers, and soil waterlogging, may have led to the decoupling of gas fluxes from the soils and interstitial gas compositions. For instance, compacted clay layers, which are typical in soil affected by hydrothermally induced alteration (del Potro and Hürlimann, 2009; Galán, 2006; Madonia et al., 2019) such as those of LFC, BdL, NP, MZ and PdU, can form horizontal soil permeability barriers limiting the soil gas effluxes and causing gas accumulation within the soil. Ploughing activities, possibly occurring at TCM, may have strongly changed local soil gas diffusivity and air permeation by modifying the soil structure (Ball et al., 2008). In addition, the numbers, species, and activities of soil microorganisms typically vary significantly in the soil as strongly influenced by many labile parameters, including: O₂ concentration (Haque et al., 2020), moisture content (Boeckx and Van Cleemput, 1996; Zhao et al., 2021), temperature (Börjesson et al., 2004; Visvanathan et al., 1999), soil pH (Kou et al., 2021), availability of nutrients (Chowdhury and Dick, 2013; Knief, 2019), soil texture and soil organic matter content (Witzgall et al., 2021). As a result, changes in these soil attributes influence unpredictably the rate of biological processes in soils. Differently, the noticeable relation between Φ (CO₂ + CH₄) and the soil concentrations of CO₂ and CH₄ observed for the SF (Fig. 4) was likely due to the general homogeneity of soil features characterising the bottom of this volcanic crater. According to these considerations, the Φ (CO₂ + CH₄) values cannot be considered as a reliable proxy to assess the residence time of the gas within the soil.

Variability in the environmental soil conditions had effects also along soil vertical profiles (Fig. 4): gas samples from NP, MZ and PdU suffered, to variable extents, a CH₄ depletion with respect to CO₂ at shallow depths, reflecting both air mixing and enhanced CH₄ oxidation due to O₂ availability, whilst at both LFC and BdL, the reciprocal levels of CH₄ and CO₂ were instead basically undistinguished indicating weak soil aeration and low methanotrophic activity, the latter presumably due to the high S fugacity in the endogenous gas emissions (Table S.1; Jiang et al., 2023). The lack of vertical trends of both CO₂ and CH₄ concentrations at TCM (Fig. 4; Table S.2), confirmed the strong dependence of their reciprocal abundance on the CH₄ conversion rates.

5.2.2. Hypogenic VOCs

Methane is generally considered one of the most reactive

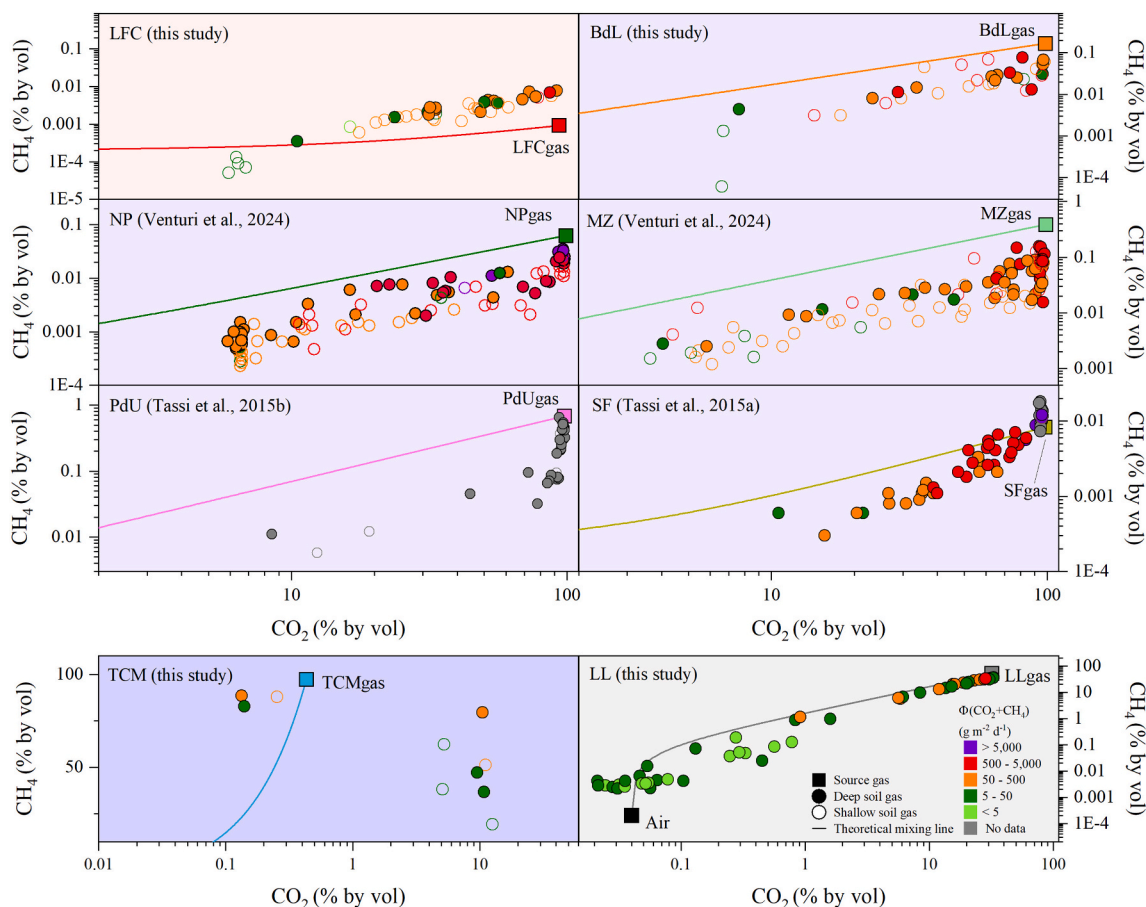


Fig. 4. CH₄ vs. CO₂ binary diagrams of soil gases from La Fossa crater (LFC), Baia di Levante (BdL), Terre Calde di Medolla (TCM), and Legoli landfill (LL; this study); Solfatara di Nepi (NP) and Caldara di Manziana (MZ; Venturi et al., 2024), Solfatara crater (SF; Tassi et al., 2015a) and Poggio dell'Ulivo (PdU; Tassi et al., 2015b). The theoretical mixing lines between hypogenic endmembers and air are also reported. Solid and open symbols represent deep and shallow soil gas samples, respectively.

hydrocarbons in the soil (Scheutz et al., 2004, 2008). Accordingly, the behaviour of the VOC groups in the different sampling sites was first assessed through the evolution of the CH₄/∑VOC_i ratios (where ∑VOC_i is the sum of specie concentrations belonging to individual VOC groups) from the hypogenic sources to soil gases. In the absence of shallow additional sources, this ratio increases in the soil gases if the considered VOC group undergo degradation at higher rates than CH₄ in the soil.

The CH₄/∑VOC_i ratios of the soil gases from the different study areas only roughly resembled those characterising the corresponding source gases and were comprised in wide ranges within the individual study areas and strongly varied along vertical soil profiles (Fig. 5). This indicated a different response of VOC groups to changing environmental conditions (from the deep source to the surface) and supported the strong influence of local soil bio-physicochemical characteristics on the extent of biogeochemical soil processes.

Owing to the large variability in the concentration and composition of gases pertaining to the different investigated systems, the comparison of the effects of biogeochemical soil processes on the hypogenic VOCs among the study areas is challenging. The normalisation of the concentrations, as a sum, of selected VOC species (∑VOC_i) computed in soil with those of the corresponding source (eq. 3) allowed to scale the values to a common range describing the extent of compositional deviations with respect to the source gas. The ∑VOC_i/∑VOC_j ratios, where ∑VOC_j is the concentration of one or the sum of selected species pertaining to the functional group of the *i* compounds or, as an alternative, to another functional organic group, were used for these computations (eq. 4): values <1 indicate either a relative depletion of

∑VOC_i or a relative enrichment of ∑VOC_j with respect to the source gas, the opposite is for values >1.

$$\text{norm} \left(\sum \text{VOC}_i \right) = \frac{\left(\sum \text{VOC}_i \right)_{\text{soil gas}}}{\left(\sum \text{VOC}_i \right)_{\text{source gas}}} \quad (3)$$

$$\text{norm} \left(\frac{\sum \text{VOC}_i}{\sum \text{VOC}_j} \right) = \frac{\left(\frac{\sum \text{VOC}_i}{\sum \text{VOC}_j} \right)_{\text{soil gas}}}{\left(\frac{\sum \text{VOC}_i}{\sum \text{VOC}_j} \right)_{\text{source gas}}} \quad (4)$$

The selection of the VOC_i-VOC_j couples was guided primarily by the identification of reactant-product relationships in the degradation reaction pathways of the target organic molecules, through an in-depth exploration of the existing empirical and theoretical investigations reported in the international literature. When potential degradation reaction pathways of such organic groups were unavailable or undetermined, we compared the relative stability of their pertaining functional groups.

5.2.2.1. Alkanes and aliphatic O-substituted compounds. The ∑alkanes-to-∑oxy (aliphatic O-substituted compounds) *norm*-ratios (i.e., $\text{norm} \left(\frac{\sum \text{ALKA}}{\sum \text{OXY}} \right)$) were mostly <1 and decreased approaching the surface along vertical soil profiles (Fig. 6a). It agreed with effective biodegradation of alkanes during the slow uprising of hypogenic gases through the soil, especially occurring in the shallowest soil strata, where O₂, i.e., the major electron acceptor, is particularly abundant. An inverse

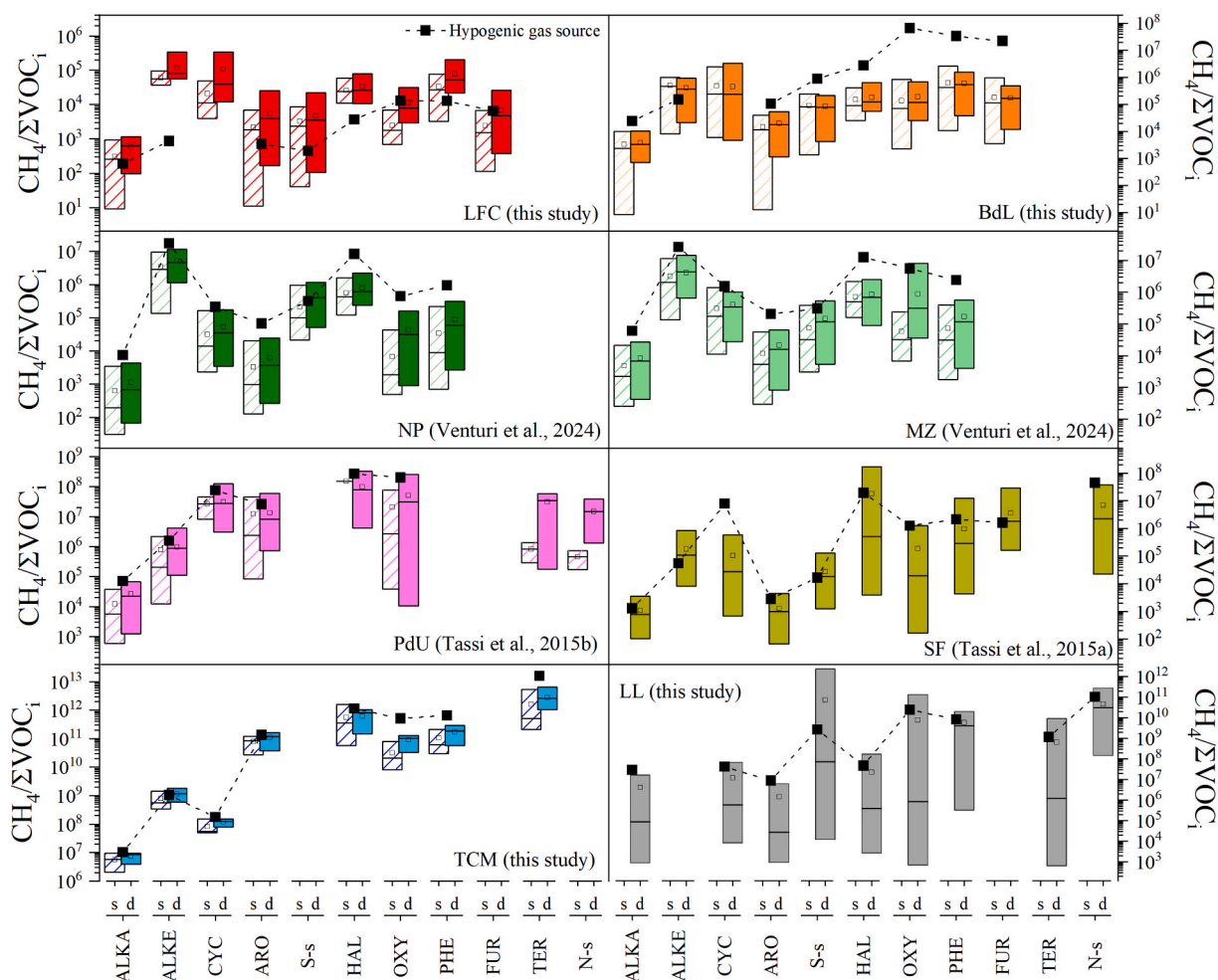


Fig. 5. Floating bar diagrams of the $\text{CH}_4/\sum\text{VOC}_i$ ratios (i = concentration of individual VOC groups) of the main functional organic groups detected in the interstitial soil gases from the investigated systems. The floating bars (line and square for median and mean values, respectively) stretch from the minimum to the maximum values. The ratio of the corresponding hypogenic source is also reported for comparison (black solid squares). The reader is referred to Fig. 3 for details of subscripts here reported. Solid colour and diagonal stripe patterns represent deep (d) and shallow (s) soil gas samples, respectively.

correlation between the contents of alkanes and aliphatic O-substituted compounds is generally expected as the extent of oxidation processes increases (Randazzo et al., 2020, 2023; Tassi et al., 2009b). Regardless of microorganisms and electron acceptors, alkane biodegradation proceeds through a series of succeeding oxidising reactions producing aliphatic O-substituted compounds (i.e., alcohols, aldehydes, organic acids, ketones and esters) as metabolites (Bian et al., 2015; Rabus et al., 2001; Rojo, 2009; Wang and Shao, 2013).

The relatively high $\text{norm}\left(\frac{\sum \text{ALKA}_{\text{C}_{5,7+}}}{\sum \text{ALKA}_{\text{C}_{2-4}}}\right)$ ratios characterising some soil gas samples from NP, MZ, PdU and LL (Fig. 6a) were possibly due to occasional secondary addition to the uprising gases of alkanes from the soil, where they likely originated from metabolic activities of living organisms, such as bacteria and fungi able to degrade plant constituents such as leaves, stems, and flowers (Choi and Lee, 2013; Randazzo et al., 2022).

As clearly shown by the $\text{norm}\left(\frac{\sum \text{ALKA}_{\text{C}_{5,7+}}}{\sum \text{ALKA}_{\text{C}_{2-4}}}\right)$ ratios in NP, MZ and SF (Fig. 6b), the degradation of alkanes proceeded to a greater extent as the chain length increases, whilst the short-chain molecules are considered relatively less reactive (Prince et al., 2007; Siddique et al., 2006). While biodegradation of short-chain alkanes ($\text{C}_2\text{-C}_4$) occurs through enzymes belonging to MMOs, biodegradation of longer-chain alkanes ($\text{C}_5\text{-C}_{17}$) is catalysed by enzymes related to cytochrome P450s and integral membrane non-heme iron monooxygenase (Wang and Shao, 2013). Hexane

generally breaks this trend due to its C_6 -structure that makes it recalcitrant compared to the other long-chain alkanes (Randazzo et al., 2020). The lack of noticeable differences in the $\text{norm}\left(\frac{\sum \text{ALKA}_{\text{C}_{5,7+}}}{\sum \text{ALKA}_{\text{C}_{2-4}}}\right)$ ratios between shallow (20 cm depth) and deep (40 cm depth) soil gases from both NP and MZ (Fig. 6b) suggested that the long-chain alkane depletion was mostly occurring below the shallower part of the soil in these systems. Differently, the $\text{norm}\left(\frac{\sum \text{ALKA}_{\text{C}_{5,7+}}}{\sum \text{ALKA}_{\text{C}_{2-4}}}\right)$ ratios of the deep soil gases from PdU and LL were, on average, consistent with those of the source gases and significantly decreased upwards along vertical soil profiles (Fig. 6b). It indicated that long-chain alkanes were generally preserved up to the shallower soil strata, where they underwent significant degradation likely caused by the establishment of thriving bacterial communities highly selective for $\text{C}_5\text{-C}_{10}$ alkanes, i.e., the ones containing the soluble CYP153 enzymes that belong to the cytochrome P450 superfamily (Van Beilen and Funhoff, 2007). The deep soil gas samples from PdU and LL characterised by $\text{norm}\left(\frac{\sum \text{ALKA}_{\text{C}_{5,7+}}}{\sum \text{ALKA}_{\text{C}_{2-4}}}\right)$ ratios > 1 (Fig. 6b) suggested intake of long-chain alkanes during the upwelling of hypogenic gases from the deep fluid source: hydrothermal alteration of buried organic matter can selectively extract long-chain alkanes depending on temperature and pressure (Petrov et al., 2021), whilst landfill gas can get enriched in long-chain alkanes by passing through different overlapped waste banks at different degrees of decomposition.

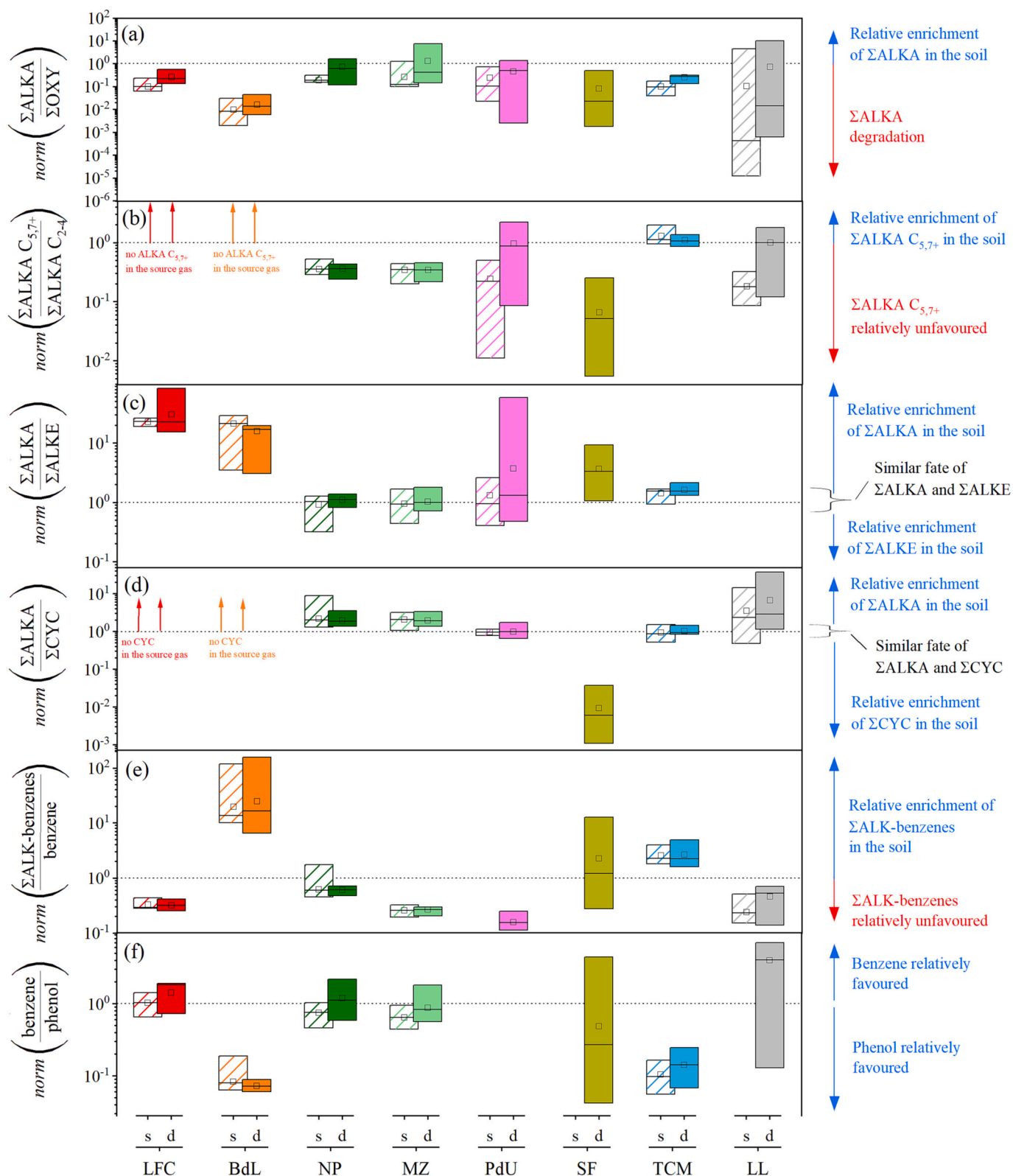


Fig. 6. Floating bar diagrams of selected *norm*-ratios computed in the interstitial soil gases from the investigated systems. The floating bars (line and square at median and mean values, respectively) stretch from the minimum to the maximum values. The reader is referred to the text (Section 5) for details of subscripts here reported and for the interpretations of the *norm*-ratios, respectively. Arrows refer to null and non-null ratios in the source and soil gases, respectively. Solid colour and diagonal stripe patterns represent deep (d) and shallow (s) soil gas samples, respectively.

No long-chain $C_{5,7+}$ alkanes were detected in fumarolic gases from LFC and BdL (Table S.1): high temperatures ($> 300\text{ }^{\circ}\text{C}$) characterising these volcanic/hydrothermal systems presumably favoured thermal cracking processes that preferentially degrade long-chain alkanes (Capaccioni et al., 1995). Accordingly, the occurrence of long-chain alkanes in the LFC and BdL soils (Table S.1) may derive by mixing with low-temperature shallow gases enriched in these VOCs from decomposition of buried organic matter (Fig. 6b). A similar explanation may also explain the $norm\left(\frac{\sum ALKA_{C_{5,7+}}}{\sum ALKA_{C_{2-4}}}\right)$ ratios >1 measured in soil gases from TCM (Fig. 6b).

5.2.2.2. Alkenes and cyclics. Although alkene and cyclic degradation at aerobic conditions is generally carried out with enzymes also supporting alkane degradation, i.e., MMOs and alkane hydroxylases (Abbasian et al., 2015; Ahmed et al., 1999; Chaîneau et al., 1995; Stepanova et al., 2022; Van Beilen and Funhoff, 2007), these organic groups behaved quite differently with respect to alkanes in the investigated soils (Fig. 6c, d). Biodegradation pathways for alkenes start from the oxidation of the subterminal or terminal methyl group to the corresponding unsaturated alcohols and organic acids (Watkinson and Morgan, 1990), while the typical biodegradation pathway for cyclohexane proceeds through a primary oxidation to the homologous alcohol that is dehydrogenated to cyclohexanone (Koma et al., 2004).

Alkanes and alkenes ($\sum ALKE$) showed a similar behaviour only in the NP, MZ and most PdU soil gases, i.e., $norm\left(\frac{\sum ALKA}{\sum ALKE}\right)$ ratios ~ 1 (Fig. 6c), whilst soil gases from the other investigated areas were marked by an enrichment in alkanes compared to the source gases ($norm\left(\frac{\sum ALKA}{\sum ALKE}\right) > 1$; Fig. 6c). This was possibly due to: (i) mixing with alkane-rich shallow source, and/or (ii) hydrogenation of alkenes during the uprising of the deep-originated gas (Cruse and Seewald, 2006; Seewald, 2001; Taran and Gigenbach, 2004), the latter hypothesis being more likely for LFC and BdL gases given the extremely high temperature expected in the gas reservoirs. Despite surface conditions tend to favour alkanes with respect to alkenes (Li et al., 2021; Tassi et al., 2012d; Zhang et al., 2019), no significant variation was observed for the $norm\left(\frac{\sum ALKA}{\sum ALKE}\right)$ ratios along vertical soil profiles. The absence of alkenes in LL soil gases was consistent with their lack in LLgas (Table S.3).

On average, only soil gases from PdU and TCM exhibited $norm\left(\frac{\sum ALKA}{\sum CYC}\right) \sim 1$ (Fig. 6d), suggesting that in these systems these organic groups were affected by secondary processes to a similar extent. Differently, in soil gases from NP, MZ and LL the $norm\left(\frac{\sum ALKA}{\sum CYC}\right)$ ratios were, on average, > 1 with no strong vertical variations along the soil profiles. It confirmed supply of alkanes from soil in NP and MZ and implied additional sources of alkanes to the uprising gases in LL, being these compounds released at relatively higher levels from degradation of organic fresh waste (Komilis et al., 2004; Randazzo et al., 2022, 2023). The larger solubility of cyclics than alkanes (Gallicchio et al., 2000) may have further contributed to the relative enrichment of alkanes in soil of NP and MZ, which host large regional aquifers (Cinti et al., 2017; Manca et al., 2017). On the contrary, SF soil gases showed $norm\left(\frac{\sum ALKA}{\sum CYC}\right)$ ratios < 1 (Fig. 6d), which have been interpreted as related to mixing with shallow circulating fluids enriched in cyclics originating from microbial activity and diagenetic processes, a process coupled with cyclic aromatisation expected in the SF gas reservoir (Tassi et al., 2015a). The occurrence of cyclic compounds in soil gases from BdL and LFC, which were not detected in the gas endmembers (Table S.1), may support

mixing with low-temperature shallow gases.

5.2.2.3. Aromatics and phenol. The $norm\left(\frac{\sum ALK-benzenes}{benzene}\right)$ ratios < 1 characterising soil gas samples from LFC, NP, MZ, PdU and LL (Fig. 6e) confirmed a higher reactivity of alkylated benzenes with respect to that of benzene (Vogt et al., 2011; Weelink et al., 2010), the latter being recalcitrant under a wide range of environmental conditions due to its stable carbon ring structure (Aihara, 1992; McCollom et al., 2001).

Accordingly, soil gases from BdL, SF and TCM showing $norm\left(\frac{\sum ALK-benzenes}{benzene}\right)$ ratios > 1 (Fig. 6e) hinted addition of alkylated benzenes from microbial transformations of lignin derivatives as well as organic matter degradation at shallow depth (Beckmann and Lloyd, 2001; Turan et al., 2007).

Under aerobic conditions, aromatics undergo biodegradation through three sequential steps involving different microbial enzymes (Díaz et al., 2013; Ladino-Orjuela et al., 2016): (i) activation of the aromatic nucleus through hydroxylation and oxygenolytic processes; (ii) breaking of the C–H chemical bonds through intradiol or extradiol (type I and II) dioxygenases; (iii) degradation of central intermediates to biomass. Anaerobic biodegradation proceeds using CO_2 , SO_4^{2-} , Fe(III), Mn(IV) and NO_3^- as terminal electron acceptors during the activation of the aromatic nucleus and follows with the de-aromatisation and ring-cleavage and then generation of biomass (Ladino-Orjuela et al., 2016; Weelink et al., 2010). As far as benzene is concerned, it can also be metabolised by anaerobic and, to a higher extent, aerobic bacteria (El-Naas et al., 2014; Foght, 2008; Hunkeler et al., 2001), proceeding through hydroxylation and formation of phenol as an intermediate metabolite, which is finally converted into the high-reactive catechol (Coates et al., 2002; Holliger and Zehender, 1996; Jindrová et al., 2002; Karich et al., 2013; Vogt et al., 2011; Weelink et al., 2010). Accordingly, the reciprocal proportions among benzene and phenol in soil depend on the rates of both benzene-phenol and phenol-catechol conversions. These processes, in their turn, depend on biochemical-physical conditions, including: (i) redox potential, (ii) temperature, (iii) concentration of the substrates, (iv) microbial community and (v) gas mixture composition (Al-Khalid and El-Naas, 2012; Coates et al., 2002; El-Naas et al., 2014; Hamed et al., 2003; Shibata et al., 2006; Vogt et al., 2011). Therefore, the general inconsistency of the $norm\left(\frac{benzene}{phenol}\right)$ ratios among investigated areas was not surprising (Fig. 6f). In contrast, the recurrent decreasing trend, except for BdL, of the $norm\left(\frac{benzene}{phenol}\right)$ ratios upwards along the vertical profiles (Fig. 6f) may suggest a relative less reactivity of benzene under high oxidising conditions.

5.2.2.4. S- and N-substituted compounds. The $norm\left(\frac{DMS}{DMSO}\right)$ ratios < 1 , shown by soil gases from LFC, BdL, SF and LL and their decreases upwards along NP and MZ vertical profiles (Fig. 7a), confirmed the high reactivity of DMS with respect to its oxidised counterpart at increasing O_2 availability (Lomans et al., 2002; Tassi et al., 2009b). Several soil microbial strains have been recognised to metabolise DMS, which can be used as either carbon or sulfur sources (Schäfer et al., 2010): the biological assimilation proceeds mainly via DMS-monoxygenase through the production of formaldehyde, which is directly assimilated into biomass or further oxidised to CO_2 , and methanethiol, which is then converted to formaldehyde, hydrogen peroxide, and sulfide. Furthermore, DMS can be converted by bacteria, including methanotrophs, to DMSO that in turn can be biologically reduced to DMS (Alef and Kleiner, 1989; Saari and Martikainen, 2003; Schäfer et al., 2010). Exceptions of NP and MZ soil gases (Fig. 7a), whose $norm\left(\frac{DMS}{DMSO}\right)$ ratios > 1 , have been ascribed to a progressive DMS intake from shallow biological processes e.g., interaction of organic compounds with H_2S or S-enriched organic matter degradation (Venturi et al., 2024).

Thiophene is known to be highly recalcitrant since no microbial

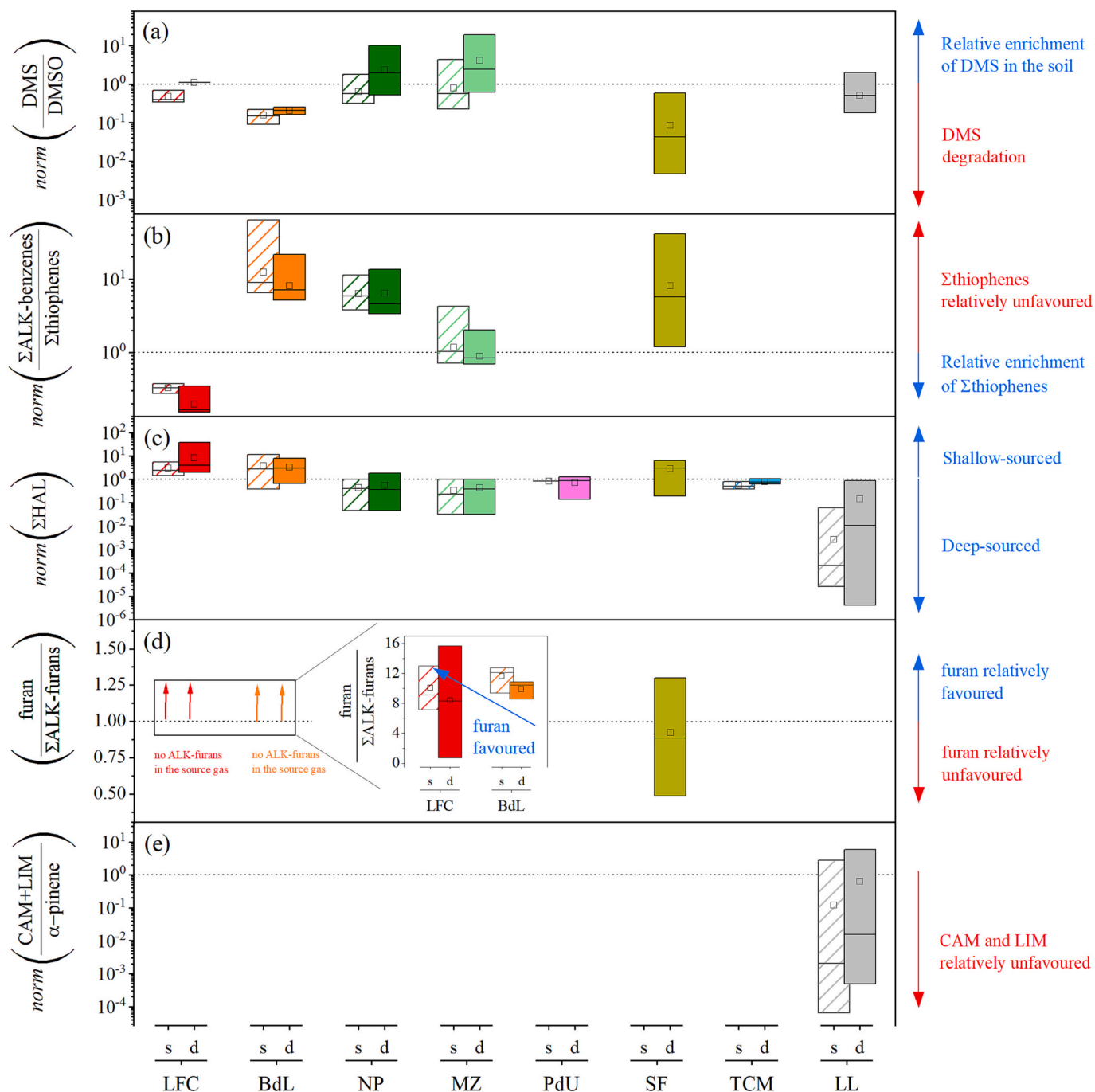


Fig. 7. Floating bar diagrams of selected *norm*-ratios computed in the interstitial soil gases from the investigated systems. The floating bars (line and square at median and mean values, respectively) stretch from the minimum to the maximum values. The reader is referred to the text (Section 5) for details of subscripts here reported and for the interpretations of the *norm*-ratios, respectively. Arrows refer to null and non-null ratios in the source and soil gases, respectively. Solid colour and diagonal stripe patterns represent deep (d) and shallow (s) soil gas samples, respectively.

strain is found to be able to grow by using it as a sole source of carbon and energy (Dyreborg et al., 1998). However, given its structural similarity with benzene, cometabolic degradation of thiophenes with aromatics as the primary substrate is expected (Dyreborg et al., 1998; Kropp and Fedorak, 1998; Rivas and Arvin, 2000). Interestingly, we observed a relative depletion of thiophenes with respect to alkylated aromatics in soil gases from BdL, NP and SF and, on average, moving from 40 to 20 cm depths in the MZ vertical soil profiles (Fig. 7b), indicating that thiophenes were more reactive than alkylated compounds. Koleva et al. (2011) have proposed a possible reaction pathway for thiophene cometabolisation from multi-level predictions based on the functional group

and biotransformation rules. It includes six subsequent steps: (i) aromatic ring hydroxylation, (ii) isomerism, (iii) aromatic ring cleavage, (iv) desulfurization, (v) hydrolysis, and (vi) decarboxylation. The *norm* ($\frac{\sum ALK-benzenes}{\sum thiophenes}$) ratios <1 characterising the LFC soil gases (Fig. 7b) may support a certain spatial variability in the composition of the feeding gas at LFC.

Benzothiazole was found only in soil gases from LL and SF (Table S.3., Tassi et al., 2015a), according with the corresponding source gases (Fig. 3). Even if some bacterial strains able to degrade

benzothiazole have been isolated (De Wever et al., 2001; De Wever and Verachtert, 1997), no evidence to bear this process was observed.

5.2.2.5. Halogenated compounds. No compositional trend from the source to the soil supported the degradation of halogenated compounds. Most of the NP, MZ, PdU, TCM and LL soil gases showed most $norm(\sum HAL) < 1$ (Fig. 7c), suggesting that halocarbons in soil were supplied by their deep source instead of atmospheric air and/or a shallow process, such as abiotic methylation of soil halogens (Keppler et al., 2000). Differently, the excesses of halogenated compounds observed for LFC, BdL and SF soil gas samples with respect to their source gases (Fig. 7c) may have been ascribed to secondary halogenation during the ascension of gases towards the surface rather than an atmospheric contribution, considering the relatively high temperatures and high fugacity of Cl and F of these systems (Jordan, 2003).

5.2.2.6. Furans. Furans were detected only in LFC, BdL and SF soil gases, consistently with the corresponding source gas composition (Fig. 3). The detection of alkylated furans ($\sum ALK\text{-furans}$) in the LFC and BdL soil gases and not in the corresponding source gases (Fig. 7d) may support a large variability in the chemical composition of the uprising geogenic gases. However, the increase of the $\left(\frac{furan}{\sum ALK\text{-furans}}\right)$ ratios upwards along the vertical soil profiles at LFC and BdL suggested recalcitrance of furan with respect to its alkylated counterpart in shallow environments (Fig. 7d). Previous studies have reported biodegradation of furans carried out by numerous microorganisms and fungi (Abdulrashid and Clark, 1987; Prajwal and Murari, 2022; Rathna et al., 2018; Zanellati et al., 2021). Differently, no significant variation in the reciprocal ratios of these compounds was observed for SF. The reason may be found in the peculiar local speciation of soil microbial communities (López et al., 2004).

5.2.2.7. Terpenes. Among terpenes, only α -pinene was detected in the PdU and TCM soil gases (Tassi et al., 2015b; Table S.2) where it was reasonably supplied by permeating air. This VOC is generally considered persistent and ubiquitous in the atmosphere, with concentrations ranging from fractions of ppb to ppm (Huang et al., 2022b; Mermet et al., 2019; Spielmann et al., 2017; Sumitomo et al., 2015), depending on the occurrence of plant species emitting α -pinene and on environmental and meteorological conditions (Loreto et al., 1996; Tripathi and Sahu, 2020). The lack of detectable amounts of α -pinene in soil gases from LFC, BdL, NP, MZ and SF (Table S.1, Tassi et al., 2015a; Venturi et al., 2024) may have been owed to a scarce production of terpenes from the surroundings arboreal and shrubby covers.

The additional occurrence of camphene (CAM) and limonene (LIM) in both LLgas and LL soil gases supported an extra-atmospheric contribution (Table S.3). Notably, the $norm\left(\frac{CAM+LIM}{\alpha\text{-pinene}}\right)$ ratios in LL soil gases were < 1 and, on average, decrease moving upwards along vertical soil profiles (Fig. 7e). Such a trend inferred a relatively high reactivity of CAM and LIM in soil, in agreement with previous studies (Perry and Gibson, 1977; Bicas et al., 2008; Duetz et al., 2003). However, α -pinene addition to the LL soil gases from the air-fresheners sprayed over the landfill surface could not be excluded.

5.2.2.8. Overview of degradation soil processes on hypogenic VOCs. Biogeochemical processes dramatically modified the composition of VOCs in the hypogenic gases permeating through the soil from deep natural sources located in different geological settings and from anthropic (municipal waste landfill) contexts. Hypogenic gases uprising from their source regions were exposed to changing physicochemical conditions and, hence, affected by a variety of environment-dependent chemical reactions mostly mediated by microbial communities (e.g., hydrogenation, dealkylation and oxidation). Under strongly changing physicochemical conditions among the investigated environment

contexts, consistencies and interesting differences were observed in the behaviour of organic hypogenic gases in soils (Fig. 8).

Alkanes, especially $C_{5,7+}$ molecules with respect to the shorter chain ones, were found to be strongly unstable within every investigated soil. Alkenes and cyclics followed the fate of alkanes, although shallow supplies of both alkanes and cyclics from biological processes did not make it clearly noticeable. Noteworthy, in the volcanic context, hypogenic alkenes got particularly unstable during the ascension towards the surface due to the drastic decrease in temperature that favoured the hydrogenation process. On the other hand, aliphatic O-substituted organic compounds (including aldehydes, esters, ketones, alcohols and organic acids), being metabolites of hydrocarbon degradation pathways, traced the ongoing degradation of geogenic VOCs. Our data confirmed the typical recalcitrance of benzene compared to its alkylated counterparts, although degradation of benzene was also hypothesised to support the relative enrichment of phenol, an intermediate in its metabolisation, especially in the shallowest layers of the soil. DMS was highly reactive in the soil, whereas its oxidised counterpart DMSO was relatively stable. Thiophenes suffered degradation soil processes to a larger extent than alkylated benzenes due to cometabolic reactions. Benzothiazole was basically preserved during the uprising of landfill gases, whilst its occurrence in natural systems was ascribed to anthropogenic contamination sources. No compositional trends were observed to support halogenated compound degradation in natural nor anthropogenic systems. Consistently with aromatics, furan exhibited a lower reactivity than alkylated furans only in volcanic systems, while in the investigated high enthalpy system no evidence supported this statement. This suggested that the temperature and the establishment of different microbial communities exerted a forcing role for furan degradation. Hypogenic terpenes only occurred in landfill gases being related to the degradation of fresh organic vegetal matter. Among them, camphene and limonene were found to be relatively more reactive than α -pinene.

Regardless of environmental contexts, transformations occurred both in the subsoil and in shallow depths, where overall hypogenic gases got relatively enriched in oxidised and lighter compounds. Soil processes acted to a variable extent in the different investigated areas and within the same systems, highlighting how local variabilities in the characteristics, physicochemical conditions and microbial communities of soil strongly constrained the patterns and proceeding of degradation processes on hypogenic VOCs. Surprisingly, the compositional differences between source and soil gases were observed to be not dependent, except for a few cases, on ΦCO_2 and ΦCH_4 values, notwithstanding these parameters are commonly considered a reliable proxy of the residence time of geogenic gases within soils.

6. Conclusions

Biogeochemical processes exhibited a pivotal control for the suites of VOCs diffusively released from volcanic, hydrothermal, and CH_4 -rich sedimentary basins, including those from landfills. As a consequence, the degradation soil processes can significantly limit the emissions into the atmosphere of hypogenic VOCs. However, potentially harmful, polluting, and toxic species pertaining to short alkanes, benzene, halogenated compounds, DMSO, benzothiazole and α -pinene remained slightly to not at all affected by soil processes whilst potentially hazardous and different oxidised compounds were produced by the degradation of hypogenic VOCs. Investigations dealing with risk assessments are claimed to evaluate the effective impact of hypogenic VOC diffusively emitted into the air on human health and the environment.

Since diffuse soil degassing has been recognised to be a major way to release geogenic gases (Etiope et al., 2002; Fischer et al., 2019; Moörner and Etiope, 2002), frequently greater than punctual gas vents, the exchanges of hypogenic VOCs in the soil-atmosphere interface may be an important driver for the global carbon cycle. Coming efforts should be focused on reliably quantifying and characterising hypogenic VOC soil

	Volcanic system	Hydrothermal systems		CH ₄ -rich sedimentary basin	Municipal waste landfill
		High enthalpy	Medium enthalpy		
Alkanes	✓ (only C _{2,3})	✓ (mostly C _{5,7+})	✓ (mostly C _{5,7+})	✓	✓ (mostly C _{5,7+})
O-substituted compounds	+	+	+	+	+
Alkenes	✓	?	✓	?	
Cyclics		?	? ✓	✓	?
Aromatics	? ✓ (mostly alkylated)	?	✓ (mostly alkylated)	?	✓ (mostly alkylated)
Phenol	? +	?	+	+	?
S-substituted compounds	✓ (DMS and thiophenes)	✓ (DMS and thiophenes)	✓ (DMS and thiophenes)		✓ (DMS)
N-substituted compound i.e., benzothiazole		✗			✗
Halogenated compounds	✗	✗	✗	✗	✗
Furans	✓ (alkylated)	?			
Terpenes					✓ (camphene and limonene)

✓ Affected by degradation processes + Products of VOCs' degradation processes ? No insights into degradation processes ✗ Not affected by degradation processes

Fig. 8. Summary of the fate of the hypogenic-sourced VOC species in soils from the investigated systems: a volcanic system (LFC) and its associated hydrothermal system (BdL); a high enthalpy hydrothermal system (SF); medium enthalpy hydrothermal systems (NP, MZ and PdU); a CH₄-rich sedimentary basin (TCM); a municipal waste landfill (LL). No grey cell means that the organic group (or species) was not detected in the hypogenic source gas.

releases as well as investigating main constraints controlling the stability of carbon compounds in soil.

The findings of the present study stress further investigations, combining geochemical, microbiological, ecological and pedological approaches to shed light on (i) the interplay between hypogenic VOCs and soil microbial communities in a wide range of physicochemical conditions and (ii) the reciprocal interconnections between soil microheterogeneities and gas mixture composition with microbial activities and hypogenic VOC biodegradation processes.

The best understanding of soil processes affecting hypogenic VOCs may lead to new insights into developing optimised biofilters for the removal of polluting and toxic VOCs from airstream or contaminated soils, posing new challenges for the treatment of recalcitrant species.

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2024.171483>.

CRedit authorship contribution statement

A. Randazzo: Writing – original draft, Methodology, Investigation,

Formal analysis, Data curation, Conceptualization. **S. Venturi:** Writing – review & editing, Investigation, Conceptualization. **F. Tassi:** Writing – review & editing, Supervision, Resources, Methodology, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

We acknowledge all the colleagues of the Department of Earth Sciences of the University of Florence (DST-UNIFI), the Institute of

Geosciences and Earth Resources of the National Research Council of Italy (CNR-IGG) and the Istituto Nazionale di Geofisica e Vulcanologia (INGV) for their valuable support, help and participation in sampling campaigns. This work belongs to the PhD research of the first author (PhD in Earth Sciences – Department of Earth Sciences of the University of Florence, 35th cycle). Belvedere Inc. and West Systems Ltd. are also thanked for their logistic support during the fieldwork at the landfill. The two anonymous reviewers are kindly acknowledged for their valuable and thoughtful comments and suggestions towards improving the manuscript.

References

- Aarnes, I., Fristad, K., Planke, S., Svensen, H., 2011. The impact of host-rock composition on devolatilization of sedimentary rocks during contact metamorphism around mafic sheet intrusions. *Geochim. Geophys. Geosyst.* 12 <https://doi.org/10.1029/2011GC003636>.
- Abbasian, F., Lockington, R., Mallavarapu, M., Naidu, R., 2015. A comprehensive review of aliphatic hydrocarbon biodegradation by bacteria. *Appl. Biochem. Biotechnol.* 176, 670–699. <https://doi.org/10.1007/s12010-015-1603-5>.
- Abdulrahid, N., Clark, D.P., 1987. Isolation and genetic analysis of mutations allowing the degradation of furans and thiophenes by *Escherichia coli*. *J. Bacteriol.* 169, 1267–1271. <https://doi.org/10.1128/jb.169.3.1267-1271.1987>.
- Ahmed, M., Smith, J.W., George, S.C., 1999. Effects of biodegradation on Australian Permian coals. *Org. Geochem.* 30, 1311–1322. [https://doi.org/10.1016/S0146-6380\(99\)00104-7](https://doi.org/10.1016/S0146-6380(99)00104-7).
- Aihara, J., 1992. Why aromatic compounds are stable molecules. *Sci. Am.* 266, 62–69. <https://www.jstor.org/stable/24938982>.
- Alef, K., Kleiner, D., 1989. Rapid and sensitive determination of microbial activity in soils and in soil aggregates by dimethylsulfoxide reduction. *Biol. Fertil. Soils* 8, 349–355. <https://doi.org/10.1007/BF00263168>.
- Al-Khalid, T., El-Naas, M.H., 2012. Aerobic biodegradation of phenols: a comprehensive review. *Crit. Rev. Environ. Sci. Technol.* 42, 1631–1690. <https://doi.org/10.1080/10643389.2011.569872>.
- Alvarez-Cohen, L., McCarty, P.L., 1991. Effects of toxicity, aeration, and reductant supply on trichloroethylene transformation by a mixed methanotrophic culture. *Appl. Environ. Microbiol.* 57, 228–235. <https://doi.org/10.1128/aem.57.1.228-235.1991>.
- Alvarez-Cohen, L., Speitel, G.E., 2001. Kinetics of aerobic cometabolism of chlorinated solvents. *Biodegradation* 12, 105–126. <https://doi.org/10.1023/A:1012075322466>.
- Amrani, A., 2014. Organosulfur compounds: molecular and isotopic evolution from biota to oil and gas. *Annu. Rev. Earth Planet. Sci.* 42, 733–768. <https://doi.org/10.1146/annurev-earth-050212-124126>.
- Arthur, C.L., Pawliszyn, J., 1990. Solid phase microextraction with thermal desorption using fused silica optical fibers. *Anal. Chem.* <https://doi.org/10.1021/ac00218a019>.
- Asensio, D., Peñuelas, J., Filella, I., Llusia, J., 2007. On-line screening of soil VOCs exchange responses to moisture, temperature and root presence. *Plant Soil* 291, 249–261. <https://doi.org/10.1007/s11104-006-9190-4>.
- Ball, B.C., Crichton, I., Horgan, G.W., 2008. Dynamics of upward and downward N₂O and CO₂ fluxes in ploughed or no-tilled soils in relation to water-filled pore space, compaction and crop presence. *Soil Tillage Res.* 101, 20–30. <https://doi.org/10.1016/j.still.2008.05.012>.
- Baubron, J.C., Allard, P., Toutain, J.P., 1990. Diffuse volcanic emissions of carbon dioxide from Vulcano Island, Italy. *Nature* 344, 51–53. <https://doi.org/10.1038/344051a0>.
- Beckmann, M., Lloyd, D., 2001. Extraction and identification of volatile organic substances (VOS) from Scottish peat cores. *Atmos. Environ.* 35, 79–86. [https://doi.org/10.1016/S1352-2310\(00\)00290-9](https://doi.org/10.1016/S1352-2310(00)00290-9).
- Behar, F., Kressmann, S., Rudkiewicz, J.L., Vandenbroucke, M., 1992. Experimental simulation in a confined system and kinetic modelling of kerogen and oil cracking. *Org. Geochem.* 19, 173–189. [https://doi.org/10.1016/0146-6380\(92\)90035-V](https://doi.org/10.1016/0146-6380(92)90035-V).
- Bhatt, P., Kumar, M.S., Mudliar, S., Chakrabarti, T., 2007. Biodegradation of chlorinated compounds - a review. *Crit. Rev. Environ. Sci. Technol.* 37, 165–198. <https://doi.org/10.1080/10643380600776130>.
- Bian, X.Y., Mbadanga, S.M., Liu, Y.F., Yang, S.Z., Liu, J.F., Ye, R.Q., Gu, J.D., Mu, B.Z., 2015. Insights into the anaerobic biodegradation pathway of n-alkanes in oil reservoirs by detection of signature metabolites. *Sci. Rep.* 5, 1–12. <https://doi.org/10.1038/srep09801>.
- Bicas, J.L., Fontanille, P., Pastore, G.M., Larroche, C., 2008. Characterization of monoterpene biotransformation in two pseudomonads. *J. Appl. Microbiol.* 105, 1991–2001. <https://doi.org/10.1111/j.1365-2672.2008.03923.x>.
- Boccaletti, M., Corti, G., Martelli, L., 2011. Recent and active tectonics of the external zone of the northern Apennines (Italy). *Int. J. Earth Sci.* 100, 1331–1348. <https://doi.org/10.1007/s00531-010-0545-y>.
- Boeckx, P., Van Cleemput, O., 1996. Methane oxidation in a neutral landfill cover soil: influence of moisture content, temperature, and nitrogen-turnover. *J. Environ. Qual.* 25, 178–183. <https://doi.org/10.2134/jeq1996.00472425002500010023x>.
- Bonini, M., Tassi, F., Feyzullayev, A.A., Aliyev, C.S., Capecciacci, F., Minissale, A., 2013. Deep gases discharged from mud volcanoes of Azerbaijan: new geochemical evidence. *Mar. Pet. Geol.* 43, 450–463. <https://doi.org/10.1016/j.marpetgeo.2012.12.003>.
- Boopathy, R., 2004. Anaerobic biodegradation of no. 2 diesel fuel in soil: A soil column study. *Bioresour. Technol.* 94, 143–151. <https://doi.org/10.1016/j.biortech.2003.12.006>.
- Börjesson, G., Sundh, I., Svensson, B., 2004. Microbial oxidation of CH₄ at different temperatures in landfill cover soils. *FEMS Microbiol. Ecol.* 48, 305–312. <https://doi.org/10.1016/j.femsec.2004.02.006>.
- Brown, R.W., Bull, I.D., Journeaux, T., Chadwick, D.R., Jones, D.L., 2021. Volatile organic compounds (VOCs) allow sensitive differentiation of biological soil quality. *Soil Biol. Biochem.* 156, 108187. <https://doi.org/10.1016/j.soilbio.2021.108187>.
- Caliro, S., Chiodini, G., Moretti, R., Avino, R., Granieri, D., Russo, M., Fiebig, J., 2007. The origin of the fumaroles of La Solfatarata (Campi Flegrei, South Italy). *Geochim. Cosmochim. Acta* 71, 3040–3055. <https://doi.org/10.1016/j.gca.2007.04.007>.
- Calogirou, A., Larsen, B.R., Kotzias, D., 1999. Gas-phase terpene oxidation products: a review. *Atmos. Environ.* 33, 1423–1439. [https://doi.org/10.1016/S1352-2310\(98\)00277-5](https://doi.org/10.1016/S1352-2310(98)00277-5).
- Capaccioni, B., Mangani, F., 2001. Monitoring of active but quiescent volcanoes using light hydrocarbon distribution in volcanic gases: the results of 4 years of discontinuous monitoring in the Campi Flegrei (Italy). *Earth Planet. Sci. Lett.* 188, 543–555. [https://doi.org/10.1016/S0012-821X\(01\)00338-7](https://doi.org/10.1016/S0012-821X(01)00338-7).
- Capaccioni, B., Martini, M., Mangani, F., 1995. Light hydrocarbons in hydrothermal and magmatic fumaroles: hints of catalytic and thermal reactions. *Bull. Volcanol.* 56, 593–600. <https://doi.org/10.1007/BF00301464>.
- Capaccioni, B., Tassi, F., Vaselli, O., 2001. Organic and inorganic geochemistry of low temperature gas discharges at the Baia di Levante beach, Vulcano Island, Italy. *J. Volcanol. Geotherm. Res.* 108, 173–185. [https://doi.org/10.1016/S0377-0273\(00\)00284-5](https://doi.org/10.1016/S0377-0273(00)00284-5).
- Capaccioni, B., Taran, Y., Tassi, F., Vaselli, O., Mangani, G., Macias, J.L., 2004. Source conditions and degradation processes of light hydrocarbons in volcanic gases: an example from El Chichón volcano (Chiapas state, Mexico). *Chem. Geol.* 206, 81–96. <https://doi.org/10.1016/j.chemgeo.2004.01.011>.
- Capaccioni, B., Tassi, F., Cremonini, S., Sciarra, A., Vaselli, O., 2015. Ground heating and methane oxidation processes at shallow depth in Terre Calde di Medolla (Italy): observations and conceptual model. *J. Geophys. Res. Solid Earth* 120, 3048–3064. <https://doi.org/10.1002/2014JB011635>.
- Capasso, G., Favara, R., Inguaggiato, S., 1997. Chemical features and isotopic composition of gaseous manifestations on Vulcano Island, Aeolian Islands, Italy: an interpretative model of fluid circulation. *Geochim. Cosmochim. Acta* 61, 3425–3440. [https://doi.org/10.1016/S0016-7037\(97\)00163-4](https://doi.org/10.1016/S0016-7037(97)00163-4).
- Cappelletti, M., Ghezzi, D., Zannoni, D., Capaccioni, B., Fedi, S., 2016. Diversity of methane-oxidizing bacteria in soils from “hot lands of medolla” (Italy) featured by anomalous high-temperatures and biogenic CO₂ emission. *Microbes Environ.* 31, 369–377. <https://doi.org/10.1264/jmsme2.ME16087>.
- Carapezza, M., Nuccio, P.M., Valenza, M., 1981. Genesis and evolution of the fumaroles of Vulcano (Aeolian Island, Italy): a geochemical model. *Bull. Volcanol.* 44, 547–563. <https://doi.org/10.1007/BF02600585>.
- Cardellini, C., Chiodini, G., Frondini, F., Granieri, D., Lewicki, J., Peruzzi, L., 2003. Accumulation chamber measurements of methane fluxes: application to volcanic-geothermal areas and landfills. *Appl. Geochem.* 18, 45–54. [https://doi.org/10.1016/S0883-2927\(02\)00091-4](https://doi.org/10.1016/S0883-2927(02)00091-4).
- Chaignaud, P., Morawe, M., Besauy, L., Kröber, E., Vuilleumier, S., Bringel, F., Kolb, S., 2018. Methanol consumption drives the bacterial chloromethane sink in a forest soil. *ISME J.* 12, 2681–2693. <https://doi.org/10.1038/s41396-018-0228-4>.
- Châfneau, C.H., Morel, J.L., Oudot, J., 1995. Microbial degradation in soil microcosms of fuel oil hydrocarbons from drilling cuttings. *Environ. Sci. Technol.* 29, 1615–1621. <https://doi.org/10.1021/es00006a027>.
- Chen, M., Zhu, X., Zhang, Y., Du, Z., Chen, X., Kong, X., Sun, W., Chen, C., 2020. Drought stress modify cuticle of tender tea leaf and mature leaf for transpiration barrier enhancement through common and distinct modes. *Sci. Rep.* 10, 1–12. <https://doi.org/10.1038/s41598-020-63683-4>.
- Chiodini, G., 2009. CO₂/CH₄ ratio in fumaroles a powerful tool to detect magma degassing episodes at quiescent volcanoes. *Geophys. Res. Lett.* 36, 4–9. <https://doi.org/10.1029/2008GL036347>.
- Chiodini, G., Frondini, F., 2001. Carbon dioxide degassing from the Albani Hills volcanic regions, Central Italy. *Chem. Geol.* 177, 67–83. [https://doi.org/10.1016/S0009-2541\(00\)00382-X](https://doi.org/10.1016/S0009-2541(00)00382-X).
- Chiodini, G., Cioni, R., Marini, L., 1993. Reactions governing the chemistry of crater fumaroles from Vulcano Island, Italy, and implications for volcanic surveillance. *Appl. Geochemistry* 8, 357–371. [https://doi.org/10.1016/0883-2927\(93\)90004-Z](https://doi.org/10.1016/0883-2927(93)90004-Z).
- Chiodini, G., Cioni, R., Marini, L., Panichi, C., 1995. Origin of the fumarolic fluids of Vulcano Island, Italy and implications for volcanic surveillance. *Bull. Volcanol.* 57, 99–110. <https://doi.org/10.1007/BF00301400>.
- Chiodini, G., Frondini, F., Raco, B., 1996. Diffuse emission of CO₂ from the Fossa crater, Vulcano Island (Italy). *Bull. Volcanol.* 58, 41–50. <https://doi.org/10.1007/s004450050124>.
- Chiodini, G., Cioni, R., Guidi, M., Raco, B., Marini, L., 1998. Soil CO₂ flux measurements in volcanic and geothermal areas. *Appl. Geochem.* 13, 543–552. [https://doi.org/10.1016/S0883-2927\(97\)00076-0](https://doi.org/10.1016/S0883-2927(97)00076-0).
- Choi, Y.J., Lee, S.Y., 2013. Microbial production of short-chain alkanes. *Nature* 502, 571–574. <https://doi.org/10.1038/nature12536>.
- Chowdhury, T.R., Dick, R.P., 2013. Ecology of aerobic methanotrophs in controlling methane fluxes from wetlands. *Appl. Soil Ecol.* 65, 8–22. <https://doi.org/10.1016/j.apsoil.2012.12.014>.
- Chu, Y.-X., Wang, J., Tian, G., He, R., 2021. Reduction in VOC emissions by intermittent aeration in bioreactor landfills with gas-water joint regulation. *Environ. Pollut.* 290, 118059. <https://doi.org/10.1016/j.envpol.2021.118059>.

- Cinti, D., Tassi, F., Procesi, M., Brusca, L., Cabassi, J., Capecciacci, F., Delgado Huertas, A., Galli, G., Grassa, F., Vaselli, O., Voltattorni, N., 2017. Geochemistry of hydrothermal fluids from the eastern sector of the Sabatini Volcanic District (Central Italy). *Appl. Geochem.* 84, 187–201. <https://doi.org/10.1016/j.apgeochem.2017.06.014>.
- Cinti, D., Procesi, M., Poncia, P.P., 2018. Evaluation of the theoretical geothermal potential of inferred geothermal reservoirs within the Vicano-Cimino and the Sabatini volcanic districts (Central Italy) by the application of the volume method. *Energies* 11. <https://doi.org/10.3390/en11010142>.
- Cleveland, C.C., Yavitt, J.B., 1997. Consumption of atmospheric isoprene in soil. *Geophys. Res. Lett.* 24, 2379–2382. <https://doi.org/10.1029/97GL02451>.
- Coates, J.D., Chakraborty, R., McInerney, M.J., 2002. Anaerobic benzene biodegradation - A new era. *Res. Microbiol.* 153, 621–628. [https://doi.org/10.1016/S0923-2508\(02\)01378-5](https://doi.org/10.1016/S0923-2508(02)01378-5).
- Conti, C., Guarino, M., Bacenetti, J., 2020. Measurements techniques and models to assess odor annoyance: a review. *Environ. Int.* 134, 105261 <https://doi.org/10.1016/j.envint.2019.105261>.
- Costa, S., Masotta, M., Gioncada, A., Pistolesi, M., Bosch, D., Scarlato, P., 2020. Magma evolution at La Fossa volcano (Vulcano Island, Italy) in the last 100 years: evidence from eruptive products and temperature gradient experiments. *Contrib. Mineral. Petrol.* 175, 1–22. <https://doi.org/10.1007/s00410-020-1669>.
- Crippa, M., Guizzardi, D., Pisoni, E., Solazzo, E., Guion, A., Muntean, M., Florczyk, A., Schiavina, M., Melchiorri, M., Hutfilter, A.F., 2021. Global anthropogenic emissions in urban areas: patterns, trends, and challenges. *Environ. Res. Lett.* 16 <https://doi.org/10.1088/1748-9326/ac00e2>.
- Cruse, A.M., Seewald, J.S., 2006. Geochemistry of low-molecular weight hydrocarbons in hydrothermal fluids from Middle Valley, northern Juan de Fuca ridge. *Geochim. Cosmochim. Acta* 70, 2073–2092. <https://doi.org/10.1016/j.gca.2006.01.015>.
- De Wever, H., Verachtert, H., 1997. Biodegradation and toxicity of benzothiazoles. *Water Res.* 31, 2673–2684. [https://doi.org/10.1016/S0043-1354\(97\)00138-3](https://doi.org/10.1016/S0043-1354(97)00138-3).
- De Wever, H., Besse, P., Verachtert, H., 2001. Microbial transformations of 2-substituted benzothiazoles. *Appl. Microbiol. Biotechnol.* 57, 620–625. <https://doi.org/10.1007/s00253-001-0842-2>.
- Díaz, E., Jiménez, J.I., Nogales, J., 2013. Aerobic degradation of aromatic compounds. *Curr. Opin. Biotechnol.* 24, 431–442. <https://doi.org/10.1016/j.copbio.2012.10.010>.
- Dieckmann, V., Ondrak, R., Cramer, B., Horsfield, B., 2006. Deep basin gas: new insights from kinetic modelling and isotopic fractionation in deep-formed gas precursors. *Mar. Pet. Geol.* 23, 183–199. <https://doi.org/10.1016/j.marpetgeo.2005.08.002>.
- Diliberto, I.S., Cangemi, M., Gagliano, A.L., Inguaggiato, S., Jacome Paz, M.P., Madonia, P., Mazot, A., Pedone, M., Pisciotta, A., 2021. Volcanic gas hazard assessment in the Baia di Levante area (Vulcano Island, Italy) inferred by geochemical investigation of passive fluid degassing. *Geosci* 11, 1–18. <https://doi.org/10.3390/geosciences11110478>.
- Duan, C., Liao, H., Wang, K., Ren, Y., 2023. The research hotspots and trends of volatile organic compound emissions from anthropogenic and natural sources: a systematic quantitative review. *Environ. Res.* 216, 114386 <https://doi.org/10.1016/j.envres.2022.114386>.
- Duan, Z., Scheutz, C., Kjeldsen, P., 2021. Trace gas emissions from municipal solid waste landfills: a review. *Waste Manag.* 119, 39–62. <https://doi.org/10.1016/j.wasman.2020.09.015>.
- Duetz, W.A., Bouwmeester, H., Van Beilen, J.B., Witholt, B., 2003. Biotransformation of limonene by bacteria, fungi, yeasts, and plants. *Appl. Microbiol. Biotechnol.* 61, 269–277. <https://doi.org/10.1007/s00253-003-1221-y>.
- Dyreborg, S., Arvin, E., Broholm, K., 1998. Concomitant aerobic biodegradation of benzene and thiophene. *Environ. Toxicol. Chem.* 17, 851–858. <https://doi.org/10.1002/etc.5620170512>.
- El-Naas, M.H., Acio, J.A., El Telib, A.E., 2014. Aerobic biodegradation of BTEX: progresses and prospects. *J. Environ. Chem. Eng.* 2, 1104–1122. <https://doi.org/10.1016/j.jece.2014.04.009>.
- Etiopie, G., Martinelli, G., 2002. Migration of carrier and trace gases in the geosphere: an overview. *Phys. Earth Planet. Inter.* 129, 185–204. [https://doi.org/10.1016/S0031-9201\(01\)00292-8](https://doi.org/10.1016/S0031-9201(01)00292-8).
- Etiopie, G., Caracausi, A., Favara, R., Italiano, F., Baci, C., 2002. Methane emission from the mud volcanoes of Sicily (Italy). *Geophys. Res. Lett.* 29, 2–5. <https://doi.org/10.1029/2001GL014340>.
- Fischer, T.P., Arellano, S., Carn, S., Aiuppa, A., Galle, B., Allard, P., Lopez, T., Shinohara, H., Kelly, P., Werner, C., Cardellini, C., Chiodini, G., 2019. The emissions of CO₂ and other volatiles from the world's subaerial volcanoes. *Sci. Rep.* 9, 1–11. <https://doi.org/10.1038/s41598-019-54682-1>.
- Foght, J., 2008. Anaerobic biodegradation of aromatic hydrocarbons: pathways and prospects. *J. Mol. Microbiol. Biotechnol.* 15, 93–120. <https://doi.org/10.1159/000121324>.
- Franklin, E.B., Alves, M.R., Moore, A.N., Kilgour, D.B., Novak, G.A., Mayer, K., Sauer, J. S., Weber, R.J., Dang, D., Winter, M., Lee, C., Cappa, C.D., Bertram, T.H., Prather, K. A., Grassian, V.H., Goldstein, A.H., 2021. Atmospheric Benzothiazoles in a coastal marine environment. *Environ. Sci. Technol.* 55, 15705–15714. <https://doi.org/10.1021/acs.est.1c04422>.
- Fredenslund, A.M., Scheutz, C., Kjeldsen, P., 2010. Tracer method to measure landfill gas emissions from leachate collection systems. *Waste Manag.* 30, 2146–2152. <https://doi.org/10.1016/j.wasman.2010.03.013>.
- Frische, M., Garofalo, K., Hansteen, T.H., Borchers, R., Harnisch, J., 2006. The origin of stable halogenated compounds in volcanic gases. *Environ. Sci. Pollut. Res.* 13, 406–413. <https://doi.org/10.1065/espr2006.01.291>.
- Galán, E., 2006. Genesis of clay minerals. *Dev. Clay Sci.* 1, 1129–1162. [https://doi.org/10.1016/S1572-4352\(05\)01042-1](https://doi.org/10.1016/S1572-4352(05)01042-1).
- Gallego, E., Roca, F.J., Perales, J.F., Sánchez, G., Esplugas, P., 2012. Characterization and determination of the odorous charge in the indoor air of a waste treatment facility through the evaluation of volatile organic compounds (VOCs) using TD-GC/MS. *Waste Manag.* 32, 2469–2481. <https://doi.org/10.1016/j.wasman.2012.07.010>.
- Gallego, E., Perales, J.F., Roca, F.J., Guardino, X., 2014. Surface emission determination of volatile organic compounds (VOC) from a closed industrial waste landfill using a self-designed static flux chamber. *Sci. Total Environ.* 470–471, 587–599. <https://doi.org/10.1016/j.scitotenv.2013.09.105>.
- Gallicchio, E., Kubo, M.M., Levy, R.M., 2000. Enthalpy-entropy and cavity decomposition of alkane hydration free energies: numerical results and implications for theories of hydrophobic solvation. *J. Phys. Chem. B* 104, 6271–6285. <https://doi.org/10.1021/jp0006274>.
- Gao, S., Zhao, P., Li, Y., Hu, J., Zhou, S., Zhang, H., Wu, J., Jiao, Z., Wang, S., Fu, Q., Zhou, B., 2021. Characterization and influence of odorous gases on the working surface of a typical landfill site: a case study in a Chinese megacity. *Atmos. Environ.* 262, 118628 <https://doi.org/10.1016/j.atmosenv.2021.118628>.
- Gershenzon, J., Dudareva, N., 2007. The function of terpene natural products in the natural world. *Nat. Chem. Biol.* 3, 408–414. <https://doi.org/10.1038/nchembio.2007.5>.
- Giggenbach, W.F., 1996. Chemical composition of volcanic gases. In: Scarpa, R., Tilling, R. (Eds.), *Monitoring and Mitigation of Volcano Hazards*. Springer, pp. 221–256. https://doi.org/10.1007/978-3-642-80087-0_7.
- Global Methane Initiative, 2023. <https://www.globalmethane.org/>. Accessed February 1st, 2023.
- Goldstein, A.H., Shaw, S.L., 2003. Isotopes of volatile organic compounds: an emerging approach for studying atmospheric budgets and chemistry. *Chem. Rev.* 103, 5025–5048. <https://doi.org/10.1021/cr0206566>.
- Gomez, E., Yan, B., Kattel, S., Chen, J.G., 2019. Carbon dioxide reduction in tandem with light-alkane dehydrogenation. *Nat. Rev. Chem.* 3, 638–649. <https://doi.org/10.1038/s41570-019-0128-9>.
- Gostner, J.M., Zeisler, J., Alam, M.T., Gruber, P., Fuchs, D., Becker, K., Neubert, K., Kleinhapp, M., Martini, S., Überall, F., 2016. Cellular reactions to long-term volatile organic compound (VOC) exposures. *Sci. Rep.* 6, 1–14. <https://doi.org/10.1038/srep37842>.
- Greenberg, J.P., Asensio, D., Turnipseed, A., Guenther, A.B., Karl, T., Gochis, D., 2012. Contribution of leaf and needle litter to whole ecosystem BVOC fluxes. *Atmos. Environ.* 59, 302–311. <https://doi.org/10.1016/j.atmosenv.2012.04.038>.
- Gu, S., Guenther, A., Faiola, C., 2021. Effects of anthropogenic and biogenic volatile organic compounds on Los Angeles air quality. *Environ. Sci. Technol.* 55, 12191–12201. <https://doi.org/10.1021/acs.est.1c01481>.
- Guenther, A., 1995. A global model of natural volatile organic compound emissions. *J. Geophys. Res.* 100, 8873–8892. <https://doi.org/10.1029/94JD02950>.
- Guenther, A., Geron, C., Pierce, T., Lamb, B., Harley, P., Fall, R., 2000. Natural emissions of non-methane volatile organic compounds, carbon monoxide, and oxides of nitrogen from North America. *Atmos. Environ.* 34, 2205–2230. [https://doi.org/10.1016/S1352-2310\(99\)00465-3](https://doi.org/10.1016/S1352-2310(99)00465-3).
- Guzmán, M.A., Márquez, G., Boente, C., Witt, C., Morato, A., Tocco, R., 2022. Geochemical evaluation of sedimentary rocks and hydrocarbon fluids in the Amistad offshore field, Progreso Basin Province, Southwest Ecuador. *J. Pet. Sci. Eng.* 213 <https://doi.org/10.1016/j.petrol.2022.110410>.
- Hamed, T.A., Bayraktar, E., Mehmetoğlu, T., Mehmetoğlu, Ü., 2003. Substrate interactions during the biodegradation of benzene, toluene and phenol mixtures. *Process Biochem.* 39, 27–35. [https://doi.org/10.1016/S0032-9592\(02\)00293-5](https://doi.org/10.1016/S0032-9592(02)00293-5).
- Hanson, R.S., Hanson, T.E., 1996. Methanotrophic bacteria. *Microbiol. Rev.* 60, 439–471. <https://doi.org/10.1128/mmr.60.2.439-471.1996>.
- Haque, M.F.U., Xu, H.J., Colin Murrell, J., Crombie, A., 2020. Facultative methanotrophy – diversity, genetics, molecular ecology and biotechnological potential: a mini-review. *Microbiol. (United Kingdom)* 166, 894–908. <https://doi.org/10.1099/mic.0.000977>.
- Holliger, C., Zehender, A.J., 1996 Jun. 1996. Anaerobic biodegradation of hydrocarbons. *Curr. Opin. Biotechnol.* 7 (3), 326–330. [https://doi.org/10.1016/S0958-1669\(96\)80039-5](https://doi.org/10.1016/S0958-1669(96)80039-5).
- Hu, G., Yu, C., Tian, X., 2014. The origin of abnormally high benzene in light hydrocarbons associated with the gas from the Kuqa depression in the Tarim Basin, China. *Org. Geochem.* 74, 98–105. <https://doi.org/10.1016/j.orggeochem.2014.01.011>.
- Hu, J.J., Wang, L., Zhang, S.P., Fu, X.H., Le, Y.Q., 2010. Optimization of electron donors to improve CO₂ fixation efficiency by a non-photosynthetic microbial community under aerobic condition using statistical experimental design. *Bioresour. Technol.* 101, 7062–7067. <https://doi.org/10.1016/j.biortech.2010.03.138>.
- Huang, D., Du, Y., Xu, Q., Ko, J.H., 2022a. Quantification and control of gaseous emissions from solid waste landfill surfaces. *J. Environ. Manag.* 302, 114001 <https://doi.org/10.1016/j.jenvman.2021.114001>.
- Huang, H., Wang, Z., Guo, J., Wang, C., Zhang, X., 2022b. Composition, seasonal variation and sources attribution of volatile organic compounds in urban air in southwestern China. *Urban Clim.* 45, 101241 <https://doi.org/10.1016/j.uclim.2022.101241>.
- Hunkeler, D., Andersen, N., Aravena, R., Bernasconi, S.M., Butler, B.J., 2001. Hydrogen and carbon isotope fractionation during aerobic biodegradation of benzene. *Environ. Sci. Technol.* 35, 3462–3467. <https://doi.org/10.1021/es0105111>.
- Irfan, A., Batool, F., Zahra Naqvi, S.A., Islam, A., Osman, S.M., Nocentini, A., Alissa, S.A., Supuran, C.T., 2020. Benzothiazole derivatives as anticancer agents. *J. Enzyme Inhib. Med. Chem.* 35, 265–279. <https://doi.org/10.1080/14756366.2019.1698036>.
- Isidorov, V.A., Zenkevich, I.G., Ioffe, B.V., 1990. Volatile organic compounds in sulfataric gases. *J. Atmos. Chem.* 10, 329–340. <https://doi.org/10.1007/BF00053867>.

- Jabłońska, J., Tawfik, D.S., 2019. The number and type of oxygen-utilizing enzymes indicates aerobic vs. anaerobic phenotype. *Free Radic. Biol. Med.* 140, 84–92. <https://doi.org/10.1016/j.freeradbiomed.2019.03.031>.
- Jiang, D., Ge, X., Lin, L., Chen, Z., Zhang, Q., Li, Y., 2023. Biological conversion of methane to methanol at high H₂S concentrations with an H₂S-tolerant methanotrophic consortium. *Renew. Energy* 204, 475–484. <https://doi.org/10.1016/j.renene.2022.12.106>.
- Jindrová, E., Chocová, M., Demnerová, K., Brenner, V., 2002. Bacterial aerobic degradation of benzene, toluene, ethylbenzene and xylene. *Folia Microbiol.* 47, 83–93. <https://doi.org/10.1007/BF02817664>.
- Jordan, A., 2003. Volcanic formation of halogenated organic compounds. *Handb. Environ. Chem.* 3, 121–139. <https://doi.org/10.1007/b10450>.
- Jordan, A., Harnisch, J., Borchers, R., Le Guern, F., Shinohara, H., 2000. Volcanogenic halocarbons. *Environ. Sci. Technol.* 34, 1122–1124. <https://doi.org/10.1021/es990838q>.
- Kadri, T., Robert, T., Rouissi, T., Sebastian, J., Magdoui, S., Brar, S.K., Martel, R., Lauzon, J.M., 2021. Column tests for evaluation of the enzymatic biodegradation capacity of hydrocarbons (C₁₀–C₅₀) contaminated soil. *Environ. Pollut.* 290, 117986. <https://doi.org/10.1016/j.envpol.2021.117986>.
- Kansal, A., 2009. Sources and reactivity of NMHCs and VOCs in the atmosphere: a review. *J. Hazard. Mater.* 166, 17–26. <https://doi.org/10.1016/j.jhazmat.2008.11.048>.
- Karich, A., Kluge, M., Ullrich, R., Hofrichter, M., 2013. Benzene oxygenation and oxidation by the peroxxygenase of *Agrocyste aegerita*. *AMB Express* 3, 1–8. <https://doi.org/10.1186/2191-0855-3-5>.
- Keita, S., Lioussé, C., Yobou, V., Dominutti, P., Guinot, B., Assamoi, E.M., Borbon, A., Haslet, S.L., Bouvier, L., Colomb, A., Coe, H., Akpo, A., Adon, J., Bahino, J., Doumbia, M., Djossou, J., Galy-Lacaux, C., Gardrat, E., Gnamien, S., Léon, J.F., Ossouhou, M., Touré N'Datchoh, E., Roblou, L., 2018. Particle and VOC emission factor measurements for anthropogenic sources in West Africa. *Atmos. Chem. Phys.* 18, 7691–7708. <https://doi.org/10.5194/acp-18-7691-2018>.
- Kepler, F., Eiden, R., Niedan, V., Pracht, J., Schöler, H.F., 2000. Halocarbons produced by natural oxidation processes during degradation of organic matter. *Nature* 403, 298–301. <https://doi.org/10.1038/35002555>.
- Kjeldsen, P., Dalager, A., Broholm, K., 1997. Attenuation of methane and nonmethane organic compounds in landfill gas affected soils. *J. Air Waste Manage. Assoc.* 47, 1268–1275. <https://doi.org/10.1080/10473289.1997.10464072>.
- Knief, C., 2019. Diversity of methane-cycling microorganisms in soils and their relation to oxygen. *Curr. Issues Mol. Biol.* 33, 23–56. <https://doi.org/10.21775/CIMB.033.023>.
- Knox, E.G., 2005. Childhood cancers and atmospheric carcinogens. *J. Epidemiol. Community Health* 59, 101–105. <https://doi.org/10.1136/jech.2004.021675>.
- Koh, S.C., Bowman, J.P., Saylor, G.S., 1993. Soluble methane monooxygenase production and trichloroethylene degradation by a type I methanotroph, *Methylomonas methanica* 68-1. *Appl. Environ. Microbiol.* 59, 960–967. <https://doi.org/10.1128/aem.59.4.960-967.1993>.
- Kokh, S.N., Sokol, E.V., Dekterev, A.A., Kokh, K.A., Rashidov, T.M., Tomilenko, A.A., Bul'bak, T.A., Khasaeva, A., Guseinov, A., 2017. The 2011 strong fire eruption of Shikhzarli mud volcano, Azerbaijan: a case study with implications for methane flux estimation. *Environ. Earth Sci.* 76, 1–20. <https://doi.org/10.1007/s12665-017-7043-5>.
- Koleva, Y.K., Petkov, P., Tasheva, Y., 2011. Prediction of the biodegradation of petroleum thiophene in the environmental. *Pet. Coal* 53, 266–274.
- Koma, D., Sakashita, Y., Kubota, K., Fujii, Y., Hasumi, F., Chung, S.Y., Kubo, M., 2004. Degradation pathways of cyclic alkanes in *Rhodococcus* sp. NDKK48. *Appl. Microbiol. Biotechnol.* 66, 92–99. <https://doi.org/10.1007/s00253-004-1623-5>.
- Komili, D.P., Ham, R.K., Park, J.K., 2004. Emission of volatile organic compounds during composting of municipal solid wastes. *Water Res.* 38, 1707–1714. <https://doi.org/10.1016/j.watres.2003.12.039>.
- Konn, C., Charlou, J.L., Holm, N.G., Mousis, O., 2015. The production of methane, hydrogen, and organic compounds in ultramafic-hosted hydrothermal vents of the mid-Atlantic ridge. *Astrobiology* 15, 381–399. <https://doi.org/10.1089/ast.2014.1198>.
- Koppmann, R., 2020. Chemistry of volatile organic compounds in the atmosphere. In: Wilkes, H. (Ed.), *Hydrocarbons, Oils and Lipids: Diversity, Origin, Chemistry and Fate*. Handbook of Hydrocarbon and Lipid Microbiology. Springer, Cham. https://doi.org/10.1007/978-3-319-90569-3_24.
- Kou, Y., Zhao, W., Liu, Y., Wu, Y., Xiao, J., Wang, X., Bing, H., Liu, Q., 2021. Diversity patterns and drivers of methanotrophic gene distributions in forest soils across a large latitudinal gradient. *Glob. Ecol. Biogeogr.* 30, 2004–2015. <https://doi.org/10.1111/geb.13362>.
- Kropp, K.G., Fedorak, P.M., 1998. A review of the occurrence, toxicity, and biodegradation of condensed thiophenes found in petroleum. *Can. J. Microbiol.* 44, 605–622. <https://doi.org/10.1139/w98-045>.
- Kuzyakov, Y., 2006. Sources of CO₂ efflux from soil and review of partitioning methods. *Soil Biol. Biochem.* 38, 425–448. <https://doi.org/10.1016/j.soilbio.2005.08.020>.
- Ladino-Orjuela, G., Gomes, E., da Silva, R., Salt, C., Parsons, J.R., 2016. Metabolic pathways for degradation of aromatic hydrocarbons by bacteria. *Rev. Environ. Contam. Toxicol.* 237, 105–121. https://doi.org/10.1007/978-3-319-23573-8_5.
- Le Mer, J., Roger, P., 2001. Production, oxidation, emission and consumption of methane by soils: a review. *Eur. J. Soil Biol.* 37, 25–50. [https://doi.org/10.1016/S1164-5563\(01\)01067-6](https://doi.org/10.1016/S1164-5563(01)01067-6).
- Lee, E.H., Park, H., Cho, K.S., 2011. Effect of substrate interaction on oxidation of methane and benzene in enriched microbial consortia from landfill cover soil. *J. Environ. Sci. Heal. - part a toxic/hazardous Subst. Environ. Eng.* 46, 997–1007. <https://doi.org/10.1080/10934529.2011.586266>.
- Leif, R.N., Simoneit, B.R.T., 1995. Ketones in hydrothermal petroleum and sediment extracts from Guaymas Basin, Gulf of California. *Org. Geochem.* 23, 889–904. [https://doi.org/10.1016/0146-6380\(95\)00085-2](https://doi.org/10.1016/0146-6380(95)00085-2).
- Leif, R.N., Simoneit, B.R.T., 2000. The role of alkenes produced during hydrous pyrolysis of a shale. *Org. Geochem.* 31, 1189–1208. <https://doi.org/10.1016/S0146-00113-3>.
- Lewis, A.C., 2018. Lewis AC. The changing face of urban air pollution. *Science* 359, 744–745. <https://doi.org/10.1126/science.aar4925>.
- Li, J.L., Zhai, X., Wu, Y.C., Wang, J., Zhang, H.H., Yang, G.P., 2021. Emissions and potential controls of light alkenes from the marginal seas of China. *Sci. Total Environ.* 758, 143655. <https://doi.org/10.1016/j.scitotenv.2020.143655>.
- Linton, M., Turnbull, A.G., 1984. Thermodynamic equilibria in the C-H system. Stability and distribution of hydrocarbon compounds. *Fuel* 63, 408–413. [https://doi.org/10.1016/0016-2361\(84\)90020-6](https://doi.org/10.1016/0016-2361(84)90020-6).
- Lomans, B.P., Van der Drift, C., Pol, A., Op den Camp, H.J.M., 2002. Microbial cycling of volatile organic sulfur compounds. *Cell. Mol. Life Sci.* 59, 575–588. <https://doi.org/10.1007/s00018-002-8450-6>.
- López, M.J., Moreno, J., Nichols, N.N., Dien, B.S., Bothast, R.J., 2004. Isolation of microorganisms for biological detoxification of lignocellulosic hydrolysates. *Appl. Microbiol. Biotechnol.* 64, 125–131. <https://doi.org/10.1007/s00253-003-1401-9>.
- Loreto, F., Ciccioli, P., Cecinato, A., Brancaleoni, E., Frattoni, M., Tricoli, D., 1996. Influence of environmental factors and air composition on the emission of α -pinene from *Quercus ilex* leaves. *Plant Physiol.* 110, 267–275. <https://doi.org/10.1104/pp.110.1.267>.
- Lun, X., Lin, Y., Chai, F., Fan, C., Li, H., Liu, J., 2020. Reviews of emission of biogenic volatile organic compounds (BVOCs) in Asia. *J. Environ. Sci. (China)* 95, 266–277. <https://doi.org/10.1016/j.jea.2020.04.043>.
- Machel, H.G., 2001. Bacterial and thermochemical sulfate reduction in diagenetic settings - old and new insights. *Sediment. Geol.* 140, 143–175. [https://doi.org/10.1016/S0037-0738\(00\)00176-7](https://doi.org/10.1016/S0037-0738(00)00176-7).
- Madonia, P., Cangemi, M., Olivares, L., Oliveri, Y., Speziale, S., Tommasi, P., 2019. Shallow landslide generation at La Fossa cone, Vulcano island (Italy): a multidisciplinary perspective. *Landslides* 16, 921–935. <https://doi.org/10.1007/s10346-019-01149-z>.
- Maesano, F.E., D'Ambrogio, C., Burrato, P., Toscani, G., 2015. Slip-rates of blind thrusts in slow deforming areas: examples from the Po plain (Italy). *Tectonophysics* 643, 8–25. <https://doi.org/10.1016/j.tecto.2014.12.007>.
- Mahlstedt, N., 2020. Thermogenic formation of hydrocarbons in sedimentary basins. In: Wilkes, H. (Ed.), *Hydrocarbons, Oils and Lipids: Diversity, Origin, Chemistry and Fate*. Springer Cham, pp. 493–522. https://doi.org/10.1007/978-3-319-90569-3_15.
- Manca, F., Viaroli, S., Mazza, R., 2017. Hydrogeology of the Sabatini Volcanic District (Central Italy). *J. Maps* 13, 252–259. <https://doi.org/10.1080/17445647.2017.1297740>.
- Mango, F.D., Hightower, J.W., James, A.T., 1994. Role of transition-metal catalysis in the formation of natural gas. *Nature* 368, 536–538. <https://doi.org/10.1038/368536a0>.
- Mattavelli, L., Novelli, L., 1988. Geochemistry and habitat of natural gases in Italy. *Org. Geochem.* 13, 1–13. [https://doi.org/10.1016/0146-6380\(88\)90021-6](https://doi.org/10.1016/0146-6380(88)90021-6).
- McCollom, T.M., 2013. Laboratory simulations of abiotic hydrocarbon formation in earth's deep subsurface. *Rev. Mineral. Geochem.* 75, 467–494. <https://doi.org/10.2138/rmg.2013.75.15>.
- McCollom, T.M., Seewald, J.S., 2006. Carbon isotope composition of organic compounds produced by abiotic synthesis under hydrothermal conditions. *Earth Planet. Sci. Lett.* 243, 74–84. <https://doi.org/10.1016/j.epsl.2006.01.027>.
- McCollom, T.M., Seewald, J.S., 2007. Abiotic synthesis of organic compounds in deep-sea hydrothermal environments. *Chem. Rev.* 107, 382–401. <https://doi.org/10.1021/cr0503660>.
- McCollom, T.M., Seewald, J.S., Simoneit, B.R.T., 2001. Reactivity of monocyclic aromatic compounds under hydrothermal conditions. *Geochim. Cosmochim. Acta* 65, 455–468. [https://doi.org/10.1016/S0016-7037\(00\)00533-0](https://doi.org/10.1016/S0016-7037(00)00533-0).
- Mermet, C., Sauvage, S., Dusanter, S., Salameh, T., Léonardis, T., Flaud, P.M., Perraudin, E., Villenave, E., Locoge, N., 2019. Optimization of a gas chromatographic unit for measuring biogenic volatile organic compounds in ambient air. *Atmos. Meas. Tech.* 12, 6153–6171. <https://doi.org/10.5194/amt-12-6153-2019>.
- Messina, P., Lathière, J., Sindelarova, K., Vuichard, N., Granier, C., Ghattas, J., Cozic, A., Hauglustaine, D.A., 2016. Global biogenic volatile organic compound emissions in the ORCHIDEE and MEGAN models and sensitivity to key parameters. *Atmos. Chem. Phys.* 16, 14169–14202. <https://doi.org/10.5194/acp-16-14169-2016>.
- Milkov, A.V., Etiope, G., 2018. Revised genetic diagrams for natural gases based on a global dataset of >20,000 samples. *Org. Geochem.* 125, 109–120. <https://doi.org/10.1016/j.orggeochem.2018.09.002>.
- Mofikoya, A.O., Yli-Pirilä, P., Kivimäenpää, M., Blande, J.D., Virtanen, A., Holopainen, J. K., 2020. Deposition of α -pinene oxidation products on plant surfaces affects plant VOC emission and herbivore feeding and oviposition. *Environ. Pollut.* 263. <https://doi.org/10.1016/j.envpol.2020.114437>.
- Montero-Montoya, R., López-Vargas, R., Arellano-Aguilar, O., 2018. Volatile organic compounds in air: sources, distribution, exposure and associated illnesses in children. *Ann. Glob. Heal.* 84, 225–238. <https://doi.org/10.29024/aogh.910>.
- Moörner, N.A., Etiope, G., 2002. Carbon degassing from the lithosphere. *Glob. Planet. Chang.* 33, 185–203. [https://doi.org/10.1016/S0921-8181\(02\)00070-X](https://doi.org/10.1016/S0921-8181(02)00070-X).
- Muennee, S., Chiemchaisri, W., Chiemchaisri, C., 2016. Enhancement of biodegradation of plastic wastes via methane oxidation in semi-aerobic landfill. *Int. Biodeterior. Biodegrad.* 113, 244–255. <https://doi.org/10.1016/j.ibiod.2016.03.016>.
- Nair, A.T., Senthilnathan, J., Nagendra, S.M.S., 2019. Emerging perspectives on VOC emissions from landfill sites: impact on tropospheric chemistry and local air quality.

- Process. Saf. Environ. Prot. 121, 143–154. <https://doi.org/10.1016/j.psep.2018.10.026>.
- NIST (National Institute of Standards and Technology), 2005. Mass Spectral Library (NIST/EPA/NIH). Gaithersburg, USA.
- Nyrop Albers, C., Kramshøj, M., Rinnan, R., 2018. Rapid mineralization of biogenic volatile organic compounds in temperate and Arctic soils. *Biogeosciences* 15, 3591–3601. <https://doi.org/10.5194/bg-15-3591-2018>.
- Pallasser, R.J., 2000. Recognizing biodegradation in gas/oil accumulations through the $\delta^{13}C$ compositions of gas components. *Org. Geochem.* 31, 1363–1373. [https://doi.org/10.1016/S0146-6380\(00\)00101-7](https://doi.org/10.1016/S0146-6380(00)00101-7).
- Pan, Q., Liu, Q., Zheng, J., Li, Y., Xiang, S., Sun, X., 2023. Volatile and semi-volatile organic compounds in landfill gas: composition characteristics and health risks. *Environ. Int.* 174, 107886 <https://doi.org/10.1016/j.envint.2023.107886>.
- Paolucci, E., Albarello, D., D'Amico, S., Lunedei, E., Martelli, L., Mucciarelli, M., Pileggi, D., 2015. A large scale ambient vibration survey in the area damaged by May–June 2012 seismic sequence in Emilia Romagna, Italy. *Bull. Earthq. Eng.* 13, 3187–3206. <https://doi.org/10.1007/s10518-015-9767-5>.
- Perry, J.J., Gibson, D.T., 1977. Microbial metabolism of cyclic hydrocarbons and related compounds. *Crit. Rev. Microbiol.* 5, 387–412. <https://doi.org/10.3109/10408417709102811>.
- Petrov, S.M., Lakhova, A.I., Safulina, A.G., Ignashev, N.E., Khelkhal, M.A., Vakhin, A.V., 2021. Conversion of organic matter of carbonate deposits in the hydrothermal fluid. *Processes* 9. <https://doi.org/10.3390/pr9111893>.
- Polonia, A., Torelli, L., Mussoni, P., Gasperini, L., Artoni, A., Klaeschen, D., 2011. The Calabrian Arc subduction complex in the Ionian Sea: regional architecture, active deformation, and seismic hazard. *Tectonics* 30, 1–28. <https://doi.org/10.1029/2010TC002821>.
- Polyakov, V.B., Horita, J., 2021. Equilibrium carbon isotope fractionation factors of hydrocarbons: semi-empirical force-field method. *Chem. Geol.* 559, 119948 <https://doi.org/10.1016/j.chemgeo.2020.119948>.
- del Potro, R., Hürlimann, M., 2009. The decrease in the shear strength of volcanic materials with argillic hydrothermal alteration, insights from the summit region of Teide stratovolcano. *Tenerife. Eng. Geol.* 104, 135–143. <https://doi.org/10.1016/j.enggeo.2008.09.005>.
- Prajwal, S., Murari, S.K., 2022. Current state, challenges, and perspectives on microbial degradation of dioxin and furan. In: Mulla, S.I., Bharagava, R.N. (Eds.), *Enzymes for Pollutant Degradation. Microorganisms for Sustainability*, Springer, pp. 247–267. https://doi.org/10.1007/978-981-16-4574-7_13.
- Prince, R.C., Parkerton, T.F., Lee, C.C., 2007. The primary aerobic biodegradation of gasoline hydrocarbons. *Environ. Sci. Technol.* 41, 3316–3321. <https://doi.org/10.1021/es062884d>.
- Rabus, R., Wilkes, H., Behrends, A., Armstroff, A., Fischer, T., Pierik, A.J., Widdel, F., 2001. Anaerobic initial reaction of n-alkanes in a denitrifying bacterium: evidence for (1-methylpentyl) succinate as initial product and for involvement of an organic radical in n-hexane metabolism. *J. Bacteriol.* 183, 1707–1715. <https://doi.org/10.1128/JB.183.5.1707-1715.2001>.
- Randazzo, A., Asensio-Ramos, M., Melián, G.V., Venturi, S., Padrón, E., Hernández, P.A., Pérez, N.M., Tassi, F., 2020. Volatile organic compounds (VOCs) in solid waste landfill cover soil: chemical and isotopic composition vs. degradation processes. *Sci. Total Environ.* 726, 138326 <https://doi.org/10.1016/j.scitotenv.2020.138326>.
- Randazzo, A., Folino, A., Tassi, F., Tatano, F., De Rosa, S., Gambioli, A., 2022. Volatile organic compounds from green waste anaerobic degradation at lab-scale: evolution and comparison with landfill gas. *Detritus* 19, 63–74. <https://doi.org/10.31025/2611-4135/2022.15188>.
- Randazzo, A., Zorzi, F., Venturi, S., Bicocchi, G., Viti, G., Tatano, F., Tassi, F., 2023. Degradation of biogas in a simulated landfill cover soil at laboratory scale: compositional changes of main components and volatile organic compounds. *Waste Manag.* 157, 229–241. <https://doi.org/10.1016/j.wasman.2022.12.027>.
- Rathna, R., Varjani, S., Nakkeeran, E., 2018. Recent developments and prospects of dioxins and furans remediation. *J. Environ. Manag.* 223, 797–806. <https://doi.org/10.1016/j.jenvman.2018.06.095>.
- Reay, D.S., Smith, P., Christensen, T.R., James, R.H., Clark, H., 2018. Methane and global environmental change. *Annu. Rev. Environ. Resour.* 43, 165–192. <https://doi.org/10.1146/annurev-environ-102017-030154>.
- Ricci, A., Cremonini, S., Severi, P., Tassi, F., Vaselli, O., Rizzo, A.L., Caracausi, A., Grassa, F., Fiebig, J., Capaccioni, B., 2023. Sources and migration pathways of methane and light hydrocarbons in the subsurface of the southern Po River basin (northern Italy). *Mar. Pet. Geol.* 147, 105981 <https://doi.org/10.1016/j.marpetgeo.2022.105981>.
- Rice, D.D., Claypool, G.E., 1981. Generation, accumulation, and resource potential of biogenic gas. *Am. Assoc. Pet. Geol. Bull.* 65, 5–25. <https://doi.org/10.1306/2f919765-16ce-11d7-8645000102c1865d>.
- Rivas, I.M., Arvin, E., 2000. Biodegradation of thiophene by cometabolism in a biofilm system. *Water Sci. Technol.* 41, 461–468. <https://doi.org/10.2166/wst.2000.0480>.
- Rojó, F., 2009. Degradation of alkanes by bacteria: Minireview. *Environ. Microbiol.* 11, 2477–2490. <https://doi.org/10.1111/j.1462-2920.2009.01948.x>.
- Saari, A., Martikainen, P.J., 2003. Dimethyl sulphoxide (DMSO) and dimethyl sulphide (DMS) as inhibitors of methane oxidation in forest soil. *Soil Biol. Biochem.* 35, 383–389. [https://doi.org/10.1016/S0038-0717\(02\)00288-2](https://doi.org/10.1016/S0038-0717(02)00288-2).
- Sánchez-Avila, J.I., García-Sánchez, B.E., Vara-Castro, G.M., Kretzschmar, T., 2021. Distribution and origin of organic compounds in the condensates from a Mexican high-temperature geothermal field. *Geothermics* 89. <https://doi.org/10.1016/j.geothermics.2020.101980>.
- Sandison, C.M., Alexander, R., Kagi, R.L., Boreham, C.J., 2003. Early diagenetic transformation of organic matter in a marine-influenced lignite. *Org. Geochem.* 34, 1081–1102. [https://doi.org/10.1016/S0146-6380\(03\)00068-8](https://doi.org/10.1016/S0146-6380(03)00068-8).
- Schäfer, H., Myronova, N., Boden, R., 2010. Microbial degradation of dimethylsulphide and related C₁-Sulphur compounds: organisms and pathways controlling fluxes of Sulphur in the biosphere. *J. Exp. Bot.* 61, 315–334. <https://doi.org/10.1093/jxb/erp355>.
- Scheutz, C., Hans, M., Kjeldsen, P., 2004. Attenuation of methane and volatile organic compounds in landfill soil covers. *J. Environ. Qual.* 33, 61–71. <https://doi.org/10.2134/jeq2004.6100>.
- Scheutz, C., Bogner, J., Chanton, J.P., Blake, D., Morcet, M., Aran, C., Kjeldsen, P., 2008. Atmospheric emissions and attenuation of non-methane organic compounds in cover soils at a French landfill. *Waste Manag.* 28, 1892–1908. <https://doi.org/10.1016/j.wasman.2007.09.010>.
- Schreiber, U., Mayer, C., Schmitz, O.J., Rosendahl, P., Bronja, A., Greule, M., Keppler, F., Mulder, I., Sattler, T., Schöler, H.F., 2017. Organic compounds in fluid inclusions of Archean quartz - analogues of prebiotic chemistry on early earth. *PLoS One* 12, 1–9. <https://doi.org/10.1371/journal.pone.0177570>.
- Schwandner, F.M., Seward, T.M., Gize, A.P., Hall, P.A., Dietrich, V.J., 2004. Diffuse emission of organic trace gases from the flank and crater of a quiescent active volcano (Vulcano, Aeolian Islands, Italy). *J. Geophys. Res. Atmos.* 109. <https://doi.org/10.1029/2003jd003890>.
- Schwandner, F.M., Seward, T.M., Gize, A.P., Hall, K., Dietrich, V.J., 2013. Halocarbons and other trace heteroatomic organic compounds in volcanic gases from Vulcano (Aeolian Islands, Italy). *Geochim. Cosmochim. Acta* 101, 191–221. <https://doi.org/10.1016/j.gca.2012.10.004>.
- Sciarra, A., Cantucci, B., Coltorti, M., 2017. Learning from soil gas change and isotopic signatures during 2012 Emilia seismic sequence. *Sci. Rep.* 7, 2–8. <https://doi.org/10.1038/s41598-017-14500-y>.
- Sciarra, A., Cantucci, B., Sapia, V., De Ritis, R., Ricci, T., Civico, R., Galli, G., Cinti, D., Coltorti, M., 2021. Geochemical and geoelectrical characterization of the Terre Calde di Medolla (Emilia-Romagna, northern Italy) and relations with 2012 seismic sequence. *J. Geochem. Explor.* 221, 106678 <https://doi.org/10.1016/j.gexplo.2020.106678>.
- Seewald, J.S., 2001. Aqueous geochemistry of low molecular weight hydrocarbons at elevated temperatures and pressures: constraints from mineral buffered laboratory experiments. *Geochim. Cosmochim. Acta* 65, 1641–1664. [https://doi.org/10.1016/S0016-7037\(01\)00544-0](https://doi.org/10.1016/S0016-7037(01)00544-0).
- Shi, Q., Wu, J., 2021. Review on sulfur compounds in petroleum and its products: state-of-the-art and perspectives. *Energy Fuel* 35, 14445–14461. <https://doi.org/10.1021/acs.energyfuel.1c02229>.
- Shibata, A., Inoue, Y., Katayama, A., 2006. Aerobic and anaerobic biodegradation of phenol derivatives in various paddy soils. *Sci. Total Environ.* 367, 979–987. <https://doi.org/10.1016/j.scitotenv.2006.01.031>.
- Shock, E.L., Canovas, P., Yang, Z., Boyer, G., Johnson, K., Robinson, K., Fecteau, K., Windman, T., Cox, A., 2013. Thermodynamics of organic transformations in hydrothermal fluids. *Rev. Mineral. Geochem.* 76, 311–350. <https://doi.org/10.2138/rmg.2013.76.9>.
- Siddique, T., Fedorak, P.M., Foght, J.M., 2006. Biodegradation of short-chain n-alkanes in oil sands tailings under methanogenic conditions. *Environ. Sci. Technol.* 40, 5459–5464. <https://doi.org/10.1021/es060993m>.
- Silk, P.J., Lonergan, G.C., Arsenaault, T.L., Boyle, C.D., 1997. Evidence of natural organochlorine formation in peat bogs. *Chemosphere* 35, 2865–2880. [https://doi.org/10.1016/S0045-6535\(97\)00347-0](https://doi.org/10.1016/S0045-6535(97)00347-0).
- Silvestre, A.J.D., Gandini, A., 2008. Terpenes: major sources, properties and applications. *Monomers, Polym. Compos. from Renew. Resour.* 17–38. <https://doi.org/10.1016/B978-0-08-045316-3.00002-8>.
- Sommaruga, C., 1984. Le ricerche geotermiche svolte a Vulcano negli anni '50. *Rend. della Soc. Ital. di Mineral. e Petrol.* 39, 355–366.
- Sonne, C., Xia, C., Dadvand, P., Targino, A.C., Lam, S.S., 2022. Indoor volatile and semi-volatile organic toxic compounds: need for global action. *J. Build. Eng.* 62, 105344 <https://doi.org/10.1016/j.jobee.2022.105344>.
- Spielmann, F.M., Langebner, S., Ghirardo, A., Hansel, A., Schnitzler, J.P., Wohlfahrt, G., 2017. Isoprene and α -pinene deposition to grassland mesocosms. *Plant Soil* 410, 313–322. <https://doi.org/10.1007/s11104-016-3009-8>.
- Stepanova, A.Y., Gladkov, E.A., Osipova, E.S., Gladkova, O.V., Tereshonok, D.V., 2022. Bioremediation of soil from petroleum contamination. *Processes* 10, 1224. <https://doi.org/10.3390/pr10061224>.
- Sumitomo, K., Akutsu, H., Fukuyama, S., Minooshima, A., Kukita, S., Yamamura, Y., Sato, Y., Hayasaka, T., Osanai, S., Funakoshi, H., Hasebe, N., Nakamura, M., 2015. Conifer-derived monoterpenes and forest walking. *Mass Spectrom.* 4, A0042. <https://doi.org/10.5702/massspectrometry.a0042>.
- Svensen, H., Planke, S., Polozov, A.G., Schmidbauer, N., Corfu, F., Podladchikov, Y.Y., Jamveit, B., 2009. Siberian gas venting and the end-Permian environmental crisis. *Earth Planet. Sci. Lett.* 277, 490–500. <https://doi.org/10.1016/j.epsl.2008.11.015>.
- Tang, J., Schurgers, G., Rinnan, R., 2019. Process understanding of soil BVOC fluxes in natural ecosystems: a review. *Rev. Geophys.* 57, 966–986. <https://doi.org/10.1029/2018RG000634>.
- Tarabusi, G., Caputo, R., 2017. The use of HVSR measurements for investigating buried tectonic structures: the Mirandola anticline, northern Italy, as a case study. *Int. J. Earth Sci.* 106, 341–353. <https://doi.org/10.1007/s00531-016-1322-3>.
- Taran, Y., Giggenbach, W., 2004. Evidence for metastable equilibrium between hydrocarbons in volcanic gases. *Water-Rock Interact.* 2–4.
- Taran, Y.A., Giggenbach, W.F., 2003. Geochemistry of light hydrocarbons in subduction-related volcanic and hydrothermal fluids. *Soc. Econ. Geol.* 10, 61–74. <https://doi.org/10.5382/SP.10.04>.
- Tassi, F., Capaccioni, B., Capecciacci, F., Vaselli, O., 2009a. Non-methane volatile organic compounds (VOCs) at El Chichón volcano (Chiapas, México): geochemical

- features, origin and behavior. *Geofis. Int.* 48, 85–95. <https://doi.org/10.22201/igeof.00167169p.2009.48.1.101>.
- Tassi, F., Montegrossi, G., Vaselli, O., Liccioli, C., Moretti, S., Nisi, B., 2009b. Degradation of C₂-C₁₅ volatile organic compounds in a landfill cover soil. *Sci. Total Environ.* 407, 4513–4525. <https://doi.org/10.1016/j.scitotenv.2009.04.022>.
- Tassi, F., Montegrossi, G., Capecciacci, F., Vaselli, O., 2010. Origin and distribution of thiophenes and furans in gas discharges from active volcanoes and geothermal systems. *Int. J. Mol. Sci.* 11, 1434–1457. <https://doi.org/10.3390/ijms11041434>.
- Tassi, F., Montegrossi, G., Vaselli, O., Morandi, A., Capecciacci, F., Nisi, B., 2011. Flux measurements of benzene and toluene from landfill cover soils. *Waste Manag. Res.* 29, 50–58. <https://doi.org/10.1177/0734242X10385609>.
- Tassi, F., Bonini, M., Montegrossi, G., Capecciacci, F., Capaccioni, B., Vaselli, O., 2012a. Origin of light hydrocarbons in gases from mud volcanoes and CH₄-rich emissions. *Chem. Geol.* 294–295, 113–126. <https://doi.org/10.1016/j.chemgeo.2011.12.004>.
- Tassi, F., Capecciacci, F., Bucciati, A., Vaselli, O., 2012b. Sampling and analytical procedures for the determination of VOCs released into air from natural and anthropogenic sources: a comparison between SPME (solid phase Micro extraction) and ST (solid trap) methods. *Appl. Geochem.* 27, 115–123. <https://doi.org/10.1016/j.apgeochem.2011.09.023>.
- Tassi, F., Capecciacci, F., Cabassi, J., Calabrese, S., Vaselli, O., Rouwet, D., Pecoraino, G., Chiodini, G., 2012c. Geogenic and atmospheric sources for volatile organic compounds in fumarolic emissions from Mt. Etna and Vulcano Island (Sicily, Italy). *J. Geophys. Res. Atmos.* 117, 1–20. <https://doi.org/10.1029/2012JD017642>.
- Tassi, F., Fiebig, J., Vaselli, O., Nocentini, M., 2012d. Origins of methane discharging from volcanic-hydrothermal, geothermal and cold emissions in Italy. *Chem. Geol.* 310–311, 36–48. <https://doi.org/10.1016/j.chemgeo.2012.03.018>.
- Tassi, F., Capecciacci, F., Giannini, L., Vougioukalakis, G.E., Vaselli, O., 2013a. Volatile organic compounds (VOCs) in air from Nisyros Island (Dodecanese archipelago, Greece): natural versus anthropogenic sources. *Environ. Pollut.* 180, 111–121. <https://doi.org/10.1016/j.envpol.2013.05.023>.
- Tassi, F., Nisi, B., Cardellini, C., Capecciacci, F., Donnini, M., Vaselli, O., Avino, R., Chiodini, G., 2013b. Diffuse soil emission of hydrothermal gases (CO₂, CH₄, and C₆H₆) at Solfatara crater (Campi Flegrei, southern Italy). *Appl. Geochem.* 35, 142–153. <https://doi.org/10.1016/j.apgeochem.2013.03.020>.
- Tassi, F., Venturi, S., Cabassi, J., Capecciacci, F., Nisi, B., Vaselli, O., 2015a. Volatile organic compounds (VOCs) in soil gases from Solfatara crater (Campi Flegrei, southern Italy): Geogenic source(s) vs. biogeochemical processes. *Appl. Geochem.* 56, 37–49. <https://doi.org/10.1016/j.apgeochem.2015.02.005>.
- Tassi, F., Venturi, S., Cabassi, J., Vaselli, O., Gelli, I., Cinti, D., Capecciacci, F., 2015b. Biodegradation of CO₂, CH₄ and volatile organic compounds (VOCs) in soil gas from the Vicano-Cimino hydrothermal system (Central Italy). *Org. Geochem.* 86, 81–93. <https://doi.org/10.1016/j.orggeochem.2015.06.004>.
- Taussi, M., Nisi, B., Vaselli, O., Maza, S., Morata, D., Renzulli, A., 2021. Soil CO₂ flux and temperature from a new geothermal area in the Cordón De Inacaliri volcanic complex (northern Chile). *Geothermics* 89, 101961. <https://doi.org/10.1016/j.geothermics.2020.101961>.
- Taylor, P., Larter, S., Jones, M., Dale, J., Horstad, I., 1997. The effect of oil-water-rock partitioning on the occurrence of alkylphenols in petroleum systems. *Geochim. Cosmochim. Acta* 61, 1899–1910. [https://doi.org/10.1016/S0016-7037\(97\)00034-3](https://doi.org/10.1016/S0016-7037(97)00034-3).
- Tian, G., Yuan, H., Mu, Y., He, C., Feng, S., 2007. Hydrothermal reactions from sodium hydrogen carbonate to phenol. *Org. Lett.* 9, 2019–2021. <https://doi.org/10.1021/ol0705970>.
- Tripathi, N., Sahu, L.K., 2020. Emissions and atmospheric concentrations of α -pinene at an urban site of India: role of changes in meteorology. *Chemosphere* 256, 127071. <https://doi.org/10.1016/j.chemosphere.2020.127071>.
- Turan, N.G., Akdemir, A., Ergun, O.N., 2007. Emission of volatile organic compounds during composting of poultry litter. *Water Air Soil Pollut.* 184, 177–182. <https://doi.org/10.1007/s11270-007-9406-0>.
- Turrini, C., Angeloni, P., Lacombe, O., Ponton, M., Roure, F., 2015. Three-dimensional seismo-tectonics in the Po Valley basin, northern Italy. *Tectonophysics* 661, 156–179. <https://doi.org/10.1016/j.tecto.2015.08.033>.
- Turrini, C., Toscani, G., Lacombe, O., Roure, F., 2016. Influence of structural inheritance on foreland-foredeep system evolution: an example from the Po valley region (northern Italy). *Mar. Pet. Geol.* 77, 376–398. <https://doi.org/10.1016/j.marpetgeo.2016.06.022>.
- Unger, N., 2014. On the role of plant volatiles in anthropogenic global climate change. *Geophys. Res. Lett.* 41, 8563–8569. <https://doi.org/10.1002/2014GL061616>.
- Van Beilen, J.B., Funhoff, E.G., 2007. Alkane hydroxylases involved in microbial alkane degradation. *Appl. Microbiol. Biotechnol.* 74, 13–21. <https://doi.org/10.1007/s00253-006-0748-0>.
- Vaselli, O., Tassi, F., Giannini, L., Capaccioni, B., Montegrossi, G., 2006. Sampling and analysis of volcanic gases. *Acta Vulcanol.* 18, 1000–1012. <https://doi.org/10.1400/93821>.
- Venturi, S., Tassi, F., Gould, I.R., Shock, E.L., Hartnett, H.E., Loran, E.D., Bockisch, C., Fecteau, K.M., Capecciacci, F., Vaselli, O., 2017. Mineral-assisted production of benzene under hydrothermal conditions: insights from experimental studies on C₆ cyclic hydrocarbons. *J. Volcanol. Geotherm. Res.* 346, 21–27. <https://doi.org/10.1016/j.jvolgeore.2017.05.024>.
- Venturi, S., Tassi, F., Magi, F., Cabassi, J., Ricci, A., Capecciacci, F., Caponi, C., Nisi, B., Vaselli, O., 2019. Carbon isotopic signature of interstitial soil gases reveals the potential role of ecosystems in mitigating geogenic greenhouse gas emissions: case studies from hydrothermal systems in Italy. *Sci. Total Environ.* 655, 887–898. <https://doi.org/10.1016/j.scitotenv.2018.11.293>.
- Venturi, S., Randazzo, A., Cabassi, J., Cinti, D., Meloni, F., Processi, M., Nisi, B., Voltattorni, N., Capecciacci, F., Ricci, T., Vaselli, O., Tassi, F., 2024. Geochemical features of volatile organic compounds (VOCs) in punctual and diffuse hydrothermal manifestations across the Sabatini Volcanic District (Latium, Italy): soil gases as message bearers from deep hydrothermal reservoirs. *Sci. Total Environ.* 912, 169047. <https://doi.org/10.1016/j.scitotenv.2023.169047>.
- Vichi, F., Ianniello, A., Frattoni, M., Imperiali, A., Esposito, G., Scianò, M.C.T., Perilli, M., Cecinato, A., 2021. Air quality assessment in the central mediterranean sea (Tyrrhenian Sea): anthropic impact and miscellaneous natural sources, including volcanic contribution, on the budget of volatile organic compounds (VOCs). *Atmosphere* 12, 1609. <https://doi.org/10.3390/atmos12121609>.
- ViDEPI, 2022. <https://www.videpi.com/videpi/videpi.asp>. Accessed February 6th, 2022.
- Viganò, A., Della Vedova, B., Ranalli, G., Martin, S., Scafidi, D., 2012. Geothermal and rheological regime in the Po plain sector of Adria (northern Italy). *Ital. J. Geosci.* 131, 228–240. <https://doi.org/10.3301/IJG.2012.09>.
- Visvanathan, C., Pokhrel, D., Cheimchaisri, W., Hettiaratchi, J.P.A., Wu, J.S., 1999. Methanotrophic activities in tropical landfill cover soils: effects of temperature, moisture content and methane concentration. *Waste Manag. Res.* 17, 313–323. <https://doi.org/10.1034/j.1399-3070.1999.00052.x>.
- Vogt, C., Kleinsteuber, S., Richnow, H.H., 2011. Anaerobic benzene degradation by bacteria. *Microb. Biotechnol.* 4, 710–724. <https://doi.org/10.1111/j.1751-7915.2011.00260.x>.
- Volkman, J.K., Rohjans, D., Rullkötter, J., Scholz-Böttcher, B.M., Liebezeit, G., 2000. Sources and diagenesis of organic matter in tidal flat sediments from the German Wadden Sea. *Cont. Shelf Res.* 20, 1139–1158. [https://doi.org/10.1016/S0278-4343\(00\)00016-9](https://doi.org/10.1016/S0278-4343(00)00016-9).
- Waked, A., Sauvage, S., Borbon, A., Gauduin, J., Pallares, C., Vagnot, M.P., Léonardis, T., Locoge, N., 2016. Multi-year levels and trends of non-methane hydrocarbon concentrations observed in ambient air in France. *Atmos. Environ.* 141, 263–275. <https://doi.org/10.1016/j.atmosenv.2016.06.059>.
- Wang, J., Wang, C., Chu, Y.X., Tian, G., He, R., 2023. Characterization of methanotrophic community and activity in landfill cover soils under dimethyl sulfide stress. *Waste Manag.* 161, 263–274. <https://doi.org/10.1016/j.wasman.2023.02.017>.
- Wang, W., Shao, Z., 2013. Enzymes and genes involved in aerobic alkane degradation. *Front. Microbiol.* 4, 1–7. <https://doi.org/10.3389/fmicb.2013.00116>.
- Watkinson, R.J., Morgan, P., 1990. Physiology of aliphatic hydrocarbon-degrading microorganisms. *Biodegradation* 1, 79–92. <https://doi.org/10.1007/BF00058828>.
- Weelink, S.A.B., van Eekert, M.H.A., Stams, A.J.M., 2010. Degradation of BTEX by anaerobic bacteria: physiology and application. *Rev. Environ. Sci. Biotechnol.* 9, 359–385. <https://doi.org/10.1007/s11057-010-9219-2>.
- Wei, W., Wang, S., Chatani, S., Klimont, Z., Cofala, J., Hao, J., 2008. Emission and speciation of non-methane volatile organic compounds from anthropogenic sources in China. *Atmos. Environ.* 42, 4976–4988. <https://doi.org/10.1016/j.atmosenv.2008.02.044>.
- Whelan, J.K., Hunt, J.M., 1983. Volatile C₁ C₈ organic compounds in sediments from the Peru upwelling region. *Org. Geochem.* 5, 13–28. [https://doi.org/10.1016/0146-6380\(83\)90012-8](https://doi.org/10.1016/0146-6380(83)90012-8).
- Witzgall, K., Vidal, A., Schubert, D.I., Höschen, C., Schweizer, S.A., Buegger, F., Pouteau, V., Chenu, C., Mueller, C.W., 2021. Particulate organic matter as a functional soil component for persistent soil organic carbon. *Nat. Commun.* 12, 1–10. <https://doi.org/10.1038/s41467-021-24192-8>.
- Yáñez-Serrano, A.M., Bourtsoukidis, E., Alves, E.G., Bauwens, M., Stavrou, T., Llusà, J., Filella, I., Guenther, A., Williams, J., Artaxo, P., Sindelarova, K., Doubalova, J., Kesselmeier, J., Peñuelas, J., 2020. Amazonian biogenic volatile organic compounds under global change. *Glob. Chang. Biol.* 26, 4722–4751. <https://doi.org/10.1111/gcb.15185>.
- Yang, S.S., Chang, H.L., 1998. Effect of environmental conditions on methane production and emission from paddy soil. *Agric. Ecosyst. Environ.* 69, 69–80. [https://doi.org/10.1016/S0167-8809\(98\)00098-X](https://doi.org/10.1016/S0167-8809(98)00098-X).
- Yang, Z., Gould, I.R., Williams, L.B., Hartnett, H.E., Shock, E.L., 2012. The central role of ketones in reversible and irreversible hydrothermal organic functional group transformations. *Geochim. Cosmochim. Acta* 98, 48–65. <https://doi.org/10.1016/j.gca.2012.08.031>.
- Zanellati, A., Spina, F., Bonaterra, M., Dinuccio, E., Varese, G.C., Scarpeci, T.E., 2021. Screening and evaluation of phenols and furans degrading fungi for the biological pretreatment of lignocellulosic biomass. *Int. Biodeterior. Biodegrad.* 161, 105246. <https://doi.org/10.1016/j.ibiod.2021.105246>.
- Zhang, W., Jiao, Y., Zhu, R., Rhew, R.C., Sun, B., Dai, H., 2021. Chloroform (CHCl₃) emissions from coastal Antarctic tundra. *Geophys. Res. Lett.* 48, e2021GL093811. <https://doi.org/10.1029/2021GL093811>.
- Zhang, X., Ding, X., Wang, X., Talifu, D., Wang, G., Zhang, Y., Abulizi, A., 2019. Volatile organic compounds in a petrochemical region in arid of NW China: chemical reactivity and source apportionment. *Atmosphere* 10, 641. <https://doi.org/10.3390/atmos10110641>.
- Zhao, Q., Wang, Y., Xu, Z., Yu, Z., 2021. How does biochar amendment affect soil methane oxidation? A review. *J. Soils Sediments* 21, 1575–1586. <https://doi.org/10.1007/s11368-021-02889-z>.
- Zuo, R., Han, K., Xu, D., Li, Q., Liu, J., Xue, Z., Zhao, X., Wang, J., 2022. Response of environmental factors to attenuation of toluene in vadose zone. *J. Environ. Manag.* 302, 113968. <https://doi.org/10.1016/j.jenvman.2021.113968>.