

Biogeochemical processes affecting Volatile Organic Compounds (VOCs) in interstitial soil gases from geogenic sources and municipal waste landfills

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INTRODUCTION

Non-methane volatile organic compounds (hereafter VOCs) are synthetically and naturally sourced organic compounds, having an initial boiling point less than or equal to 250°C measured at a standard pressure of 101.3 kPa, as defined by the Directive 2004/42/CE. Owing to their high volatility, VOCs are inevitably emitted into the atmosphere. Atmospheric VOCs are generated mostly by (i) biogenic and, secondarily, by (ii) geogenic, and (iii) anthropogenic processes. The contribution of geogenic VOCs is mostly related to volcanic/hydrothermal degassing and surficial seepages from deep oil and natural gas deposits. Among the anthropogenic sources, municipal waste (MW) landfills represent a major concern given the projected increase of MW generation in the next future (Chen et al., 2020). Geogenic and landfill gases comprise different cocktails of VOCs including alkane, alkene, aromatic, cyclic, terpene, halogenated and O-, Cl-, N- and S-substituted compounds (Tassi et al., 2009, 2015a). Most of these VOCs have severe impacts on the environment, air quality and human health (Gallego et al., 2012; Nair et al., 2019).

Emerging evidence has shown that soils may be powerful drivers for the global VOC cycle by acting as a sink or source (Insam and Seewald, 2010; Peñuelas et al., 2014). Soil VOC uptake occurs through mutual interactions between (i) abiotic factors, depending on physicochemical soil characteristics, and (ii) biological processes driven by microbes that use VOCs as a carbon source (Tang et al., 2019). Whilst the rapid uprising of hypogenic gases (i.e., geogenic and landfill gas) is presumed to best preserve their chemical composition up to the surface (Tassi et al., 2015b), the slow-moving through the soil is expected to exacerbate VOC compositional changes due to the long-lasting stay of the hypogenic gases at physicochemical conditions markedly different from those of their genetic environments. However, how these hypogenic VOCs respond to biogeochemical soil processes and whether soil acts as a sink for these VOCs is poorly understood so far.

According to these considerations, this study, based on fieldwork and laboratory experiments, aims to investigate biodegradation mechanisms regulating the fates of VOCs in soils affected by inputs of extra-atmospheric gases from natural and anthropic systems. Fieldwork was carried out to find out whether soil processes affecting VOCs depend on (i) the hypogenic gas composition and soil chemical-physical conditions, (ii) the residence time of uprising gases within the soil, and (iii) O₂ availability. Laboratory experiments were devoted to deeply investigating VOCs in MW landfill systems.

FIELDWORK

Study areas

The effects of the biogeochemical processes affecting hypogenic gas composition within the soil were examined by selecting six different study areas in Italy, encompassing different geological settings and a representative MW landfill, as follows: (i) an active volcanic system i.e., La Fossa Crater (LFC) associated with a high enthalpy hydrothermal system i.e., Baia di Levante (BdL) in Vulcano Island (the Aeolian Archipelago, southern Italy), which is affected by large CO₂-dominated degassing; (ii) two medium-to-high enthalpy hydrothermal systems i.e., Solfatara di Nepi (SdN) and Caldara di Manziana (CdM) belonging to the Sabatini Volcanic District (central Italy), which is characterised by CO₂-dominated diffuse emissions; (iii) a CH₄-seepage at Terre Calde di Medolla (TCM), pertaining to the CH₄-rich sedimentary basin of Po plain (northern Italy); an MW landfill, i.e., Belvedere Inc. landfill (LL) sited in Peccioli (Central Italy), characterised by landfill gas (dominated by CO₂ and CH₄) leakages.

Materials and methods

Fieldwork was based on the measurement of different geochemical parameters from a total of about 200 sampling sites properly selected to cover, as much as possible, the spatial variabilities of the study areas, as follows: (i) $\Phi(\text{CO}_2 + \text{CH}_4)$ i.e., soil CO₂ and CH₄ fluxes that were

conveniently used as a proxy for the residence time of gases within the soil; (ii) isotope ($^{13}\text{C}/^{12}\text{C}$ in CO_2 and CH_4 i.e., $\delta^{13}\text{C}\text{-CO}_2$ and $\delta^{13}\text{C}\text{-CH}_4$, respectively) and chemical compositions of inorganic volatiles and VOCs from (1) interstitial soil gases collected at two selected depths (overall in the interval depth from 60 cm depth to the effective emission into the atmosphere) along vertical soil profiles in which shallow depths were expected to be more oxidising than the deeper depths, and (2) gas vents (e.g., fumaroles, bubbling pools, dry vents) and landfill gas from a recovery well as representatives of the source gas composition of the study areas. About 500 soil gas samples were analysed and more than 20,000 data were produced. Gas analyses were conducted at the Laboratory of Fluid Geochemistry of the Department of Earth Sciences of Florence (University of Florence).

Results and discussion

Source gas composition

The different sources of gases from the investigated systems were clearly distinguished by correlating the total concentration of VOCs (ΣVOCs) with the $\text{CH}_4/(\text{C}_2\text{H}_6+\text{C}_3\text{H}_8)$ ratio (Fig. 1), which is commonly used for discerning the genetic pathways of light hydrocarbons, since biogenic gases have typically ratios $>1,000$, whilst values <100 are generally ascribed to thermogenesis (Whiticar, 1999). The ΣVOCs values decreased at increasing temperatures of the associated system, confirming that temperature favours the reactivity of VOCs (Capacioni *et al.*, 1995). On the other hand, the generation of hydrocarbons at LL and TCM is exacerbated by the large abundance of organic matter expected in their genetic environments (Randazzo *et al.*, 2020; Sherwood Lollar *et al.*, 2002). The $\text{CH}_4/(\text{C}_2\text{H}_6+\text{C}_3\text{H}_8)$ ratios were consistent with the biogenic origin, with the sole exception of CdM that falls in an intermediate interval between biogenesis

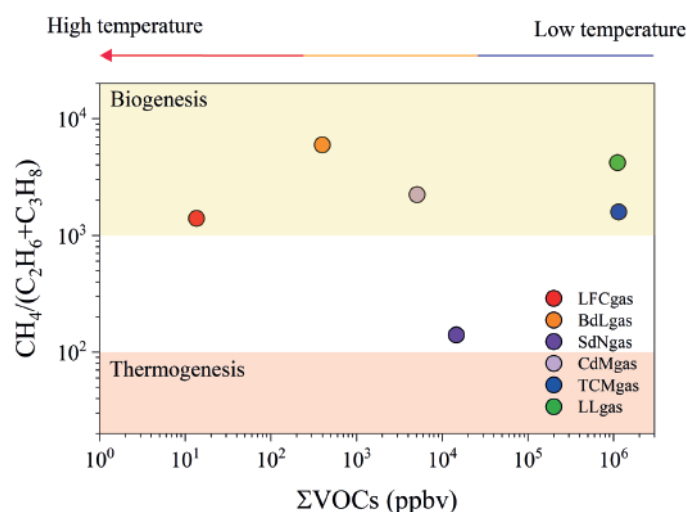


Figure 1 $\text{CH}_4/(\text{C}_2\text{H}_6+\text{C}_3\text{H}_8)$ ratio vs total concentration of VOCs (ΣVOCs , expressed as ppbv) of gas vents from La Fossa Crater (LFCgas), Baia di Levante (BdLgas), Solfatarà di Nepi (SdNgas), Caldara di Manziàna (CdMgas), Terre Calde di Medolla (TCMgas), and landfill gas from Legoli landfill (LLgas).

and thermogenesis (Fig. 1). Actually, a biogenic origin is plausible only for the cold LL and TCM systems. In fact, the relatively high temperature characterising the terrains of volcanic/hydrothermal systems hinders microbial activities (Colwell *et al.*, 1997). Accordingly, the apparent biogenic signature of volcanic and hydrothermal gases is to be ascribed to secondary processes, such as the dehydrogenation of light alkanes that is favoured under hydrothermal and volcanic conditions (Fiebig *et al.*, 2013).

The chemical VOC composition of source gases significantly differed among the investigated systems (Fig. 2), reflecting differences in the environmental conditions of the pertaining reservoir, mostly the quality and quantity of degrading organic matter, temperature, and redox state.

Controls on hypogenic CO_2 and CH_4 in soil

Overall, most soil gases, except for those of LFC, got depleted in CH_4 with respect to CO_2 compared to the expected theoretical mixing line between air and the corresponding source gases. This clearly reflects the CH_4 -to- CO_2 oxidation by methanotrophic bacteria mostly occurring within the soil, where O_2 is available (Le Mer & Roger, 2001). Differently, LFC gas samples got relatively enriched in CH_4 compared to their source gas, suggesting that the feeding gas at LFC soil was a mixture between gases from the volcanic source and a low-temperature CH_4 -enriched endmember.

It is commonly accepted that high $\Phi(\text{CO}_2+\text{CH}_4)$ values limit soil processes, decreasing their residence time within the soil, whilst low $\Phi(\text{CO}_2+\text{CH}_4)$ values favour chemical changes in the hypogenic gas composition (Randazzo *et al.*, 2020). Actually, the CO_2/CH_4 ratios of interstitial gases were not (or only roughly) related to $\Phi(\text{CO}_2+\text{CH}_4)$ values, suggesting a weak dependence of CH_4 -to- CO_2 oxidation processes on the $\Phi(\text{CO}_2+\text{CH}_4)$ values. This may have been related to spatial soil inhomogeneities, including physicochemical-biological characteristics, local permeability barriers, and waterlogging.

Neither $\delta^{13}\text{C}\text{-CO}_2$ nor $\delta^{13}\text{C}\text{-CH}_4$ trends were observed in the soil. This is to be ascribed to multiple, interdependent, local, isotope fractionation processes occurring in soil, including: (i) the CH_4 -to- CO_2 oxidation; (ii) autotrophic and heterotrophic respiration; (iii) rate, extent, and pattern of organic matter degradation processes; (iv) mixing with air or shallow-sourced gases; (v) carbon isotope exchanges at high temperature.

Soil biogeochemical mechanisms affecting hypogenic-sourced VOCs

Biogeochemical processes occurring within the soil affected to different extents the various types of hypogenic VOCs whose composition significantly changed during their transfer through the soil (Fig. 2). Biochemical degradation pathways within the soils from different stu-

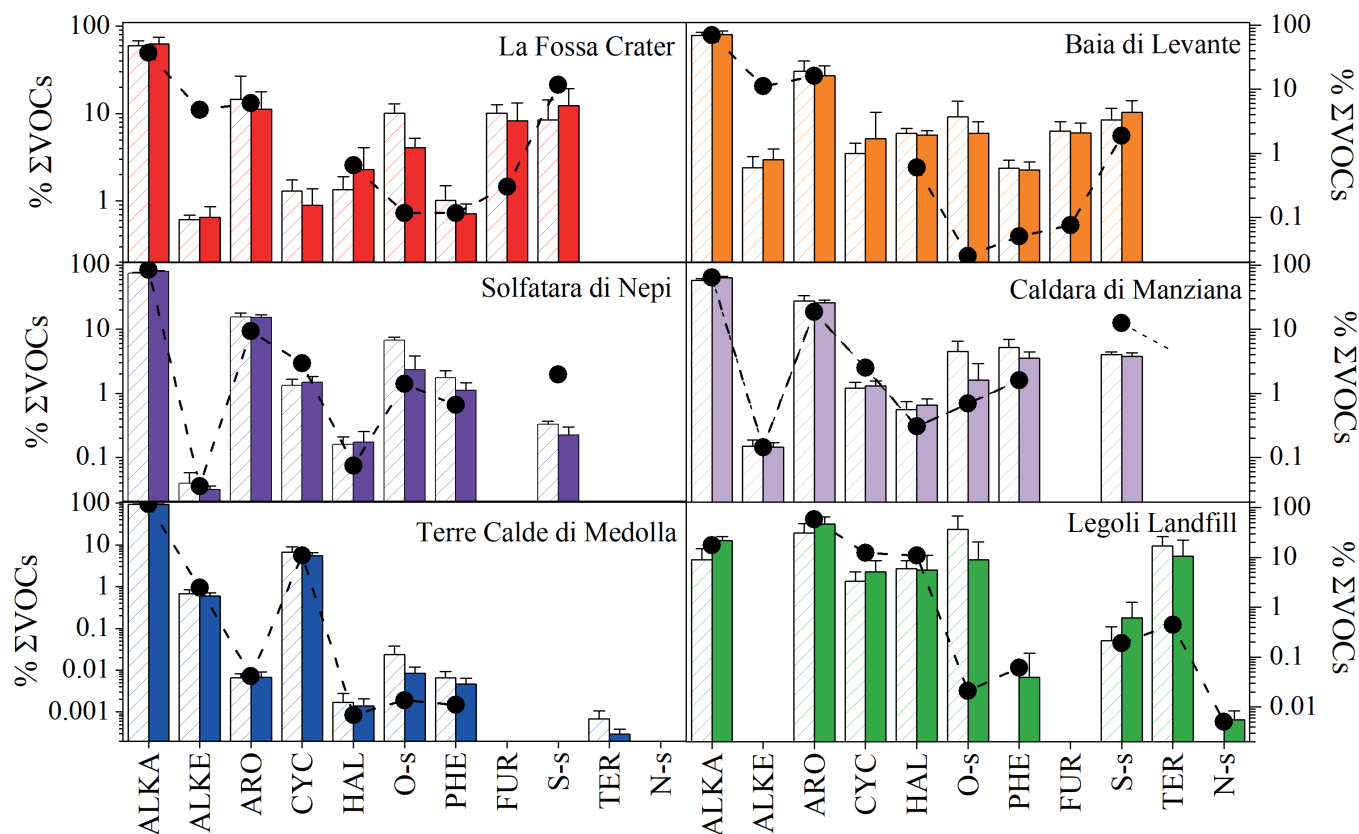


Figure 2 Bar charts representing the mean and standard deviation of the organic group concentrations (expressed as % Σ VOCs) detected in shallow (diagonal line texture) and deep (filled column) soil gas samples. Circle symbols indicate the relative abundance of the organic groups in the source gases. Legend: ALKA = alkanes; ALKE = alkenes; ARO = aromatics; CYC = cyclics; HAL = halogenated compounds; O-s = O-substituted compounds; PHE = phenol; FUR = furans; S-s = S-substituted compounds; TER = terpenes; N-s = N-substituted compound i.e., benzothiazole

dy areas showed important similarities and interesting differences.

The aerobic biodegradation of alkanes is well documented to proceed through the production of O-substituted compounds (Rojo, 2009). Consistently, most soil gases were enriched in O-substituted compounds (Σ OXY, including aldehydes, esters, ketones, and alcohols) and depleted in alkanes (Σ ALKA) respect to the corresponding gas source (Fig. 3). The excess in alkanes exhibited by some SdN and CdM soil gases was interpreted as due to mixing with low-temperature shallow gases. Also, lines of evidence have reported that branched alkanes are harder to degrade than n-alkanes (Brzeszcz & Kaszycki, 2018). The depletion of long-chain alkanes (Σ ALK-AC₅-C₇-C₈) on the short-chain ones (Σ ALK-AC₂-C₃-C₄) in soil with respect to the source gas was clearly observed for SdN and CdM soil gases, with no noticeable difference from deep to shallow soil gases, and LL soil gases, which showed a strong depletion of long-chain alkanes only at the shallowest depth (Fig. 4). This suggests that at SdN and CdM the large depth of the gas source (located at about 3,000 km depth) implied the most long-chain alkane depletion occurred before they reached the soil, whereas at LL, the proximity of the gas source (few meters) preserved long-chain alkanes almost up to the surface. The occurrence of long-chain alkanes in soil gases from LFC and BdL and not in their source gases (Fig. 4)

suggests that they were effectively cracked at relatively high temperature (Capaccioni et al., 1995), implying mixing with low-temperature shallow gases. A further source of long-chain alkanes has to be also invoked for TCM (Fig. 4). The relatively low reactivity of hexane compared to the long-chain alkanes provided by the C₆-structure was confirmed (Randazzo et al., 2020).

Our data also showed strong correlations between the total contents of alkanes and those of both cyclics and alkenes in soil gases that may support a similar reactivity of aliphatic hydrocarbons (Watkinson & Morgan, 1990). Nevertheless, a relative enrichment of alkanes on alkenes in soil gases from BdL and LFC compared to their source gases was seen, presumably caused by the hydrogenation of alkenes during the gas uprising triggered by temperature drop (Seewald, 2001). Similarly, we also observed a relative enrichment of alkanes on cyclics in soil gases from SdN, CdM, and LL that may suggest that cyclics are generally less stable than alkanes.

Cogent evidence has stated that aromatics can undergo biogeochemical degradation in soil (Díaz et al., 2013; Weelink et al., 2010). In particular, alkylated benzenes are considered relatively more reactive than benzene (Weelink et al., 2010). Consistently, soil gases from LFC, SdN, CdM, and LL were relatively enriched in benzene with respect to the source gases and the Benzene/ Σ Alkyl-benzenes ratios rose upwards along the ver-

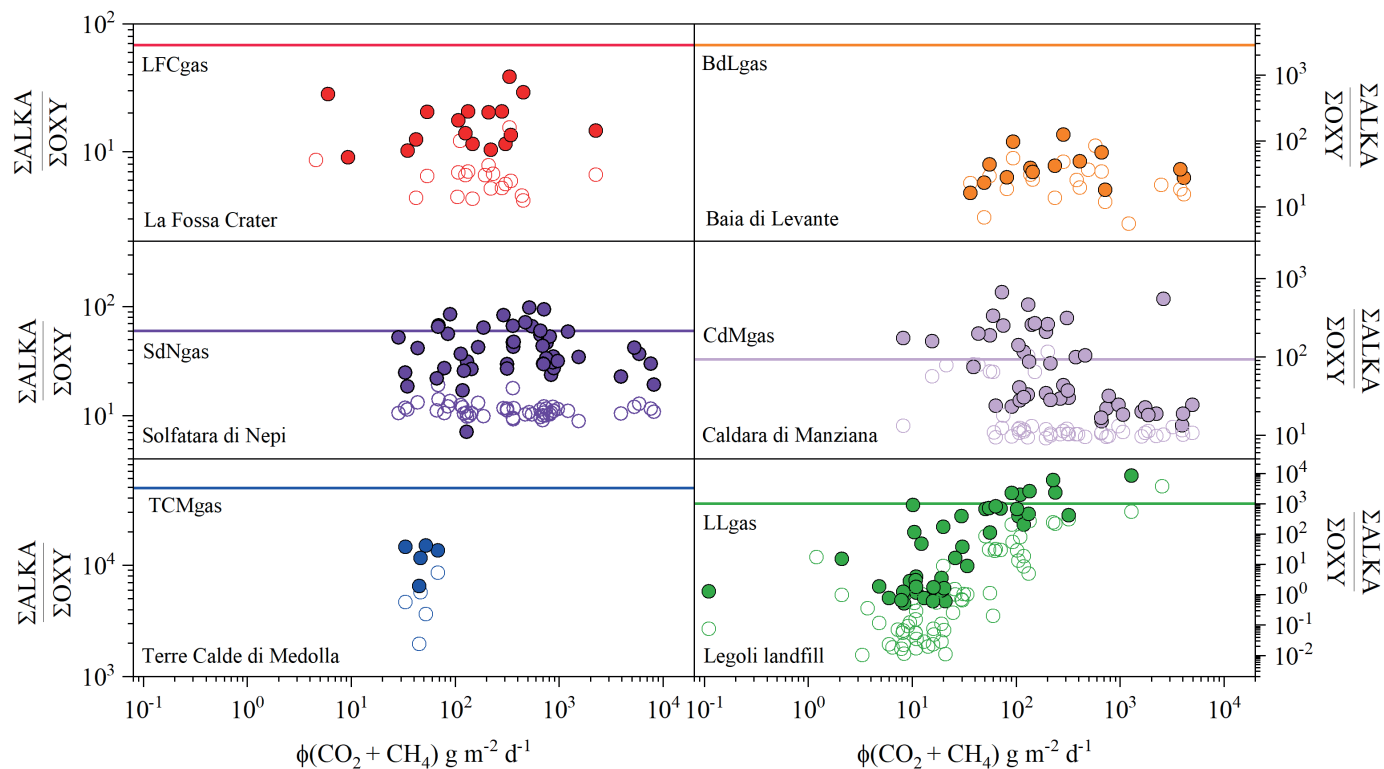


Figure 3 Binary diagrams of the ratios of alkanes (Σ ALK) on O-substituted compounds (Σ OXY) in soil gases. The Σ ALK/ Σ OXY ratios of the source gases are also reported (bold lines). Solid and open symbols represent deep and shallow soil gas samples, respectively.

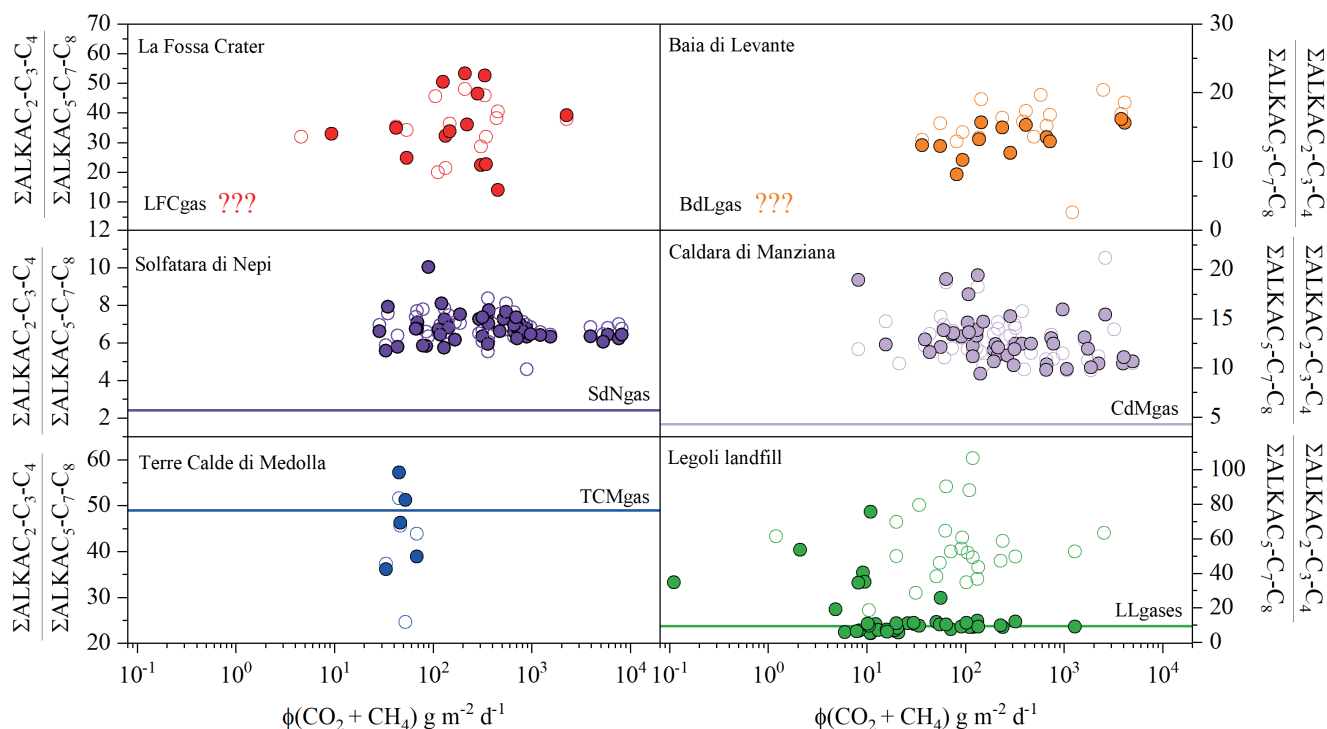


Figure 4 Binary diagrams of the ratios of short-chain alkanes (Σ ALKAC₂-C₃-C₄) on long-chain alkanes (Σ ALKAC₅-C₇-C₈) in soil gases. The Σ ALKAC₂-C₃-C₄/ Σ ALKAC₅-C₇-C₈ ratios of the source gases are also reported (bold lines). Solid and open symbols represent deep and shallow soil gas samples, respectively. The Σ ALKAC₂-C₃-C₄/ Σ ALKAC₅-C₇-C₈ ratios of the source gases from La Fossa Crater and Baia di Levante were not computed due to the lack of long-chain alkanes

tical profiles in LL and CdM (Fig. 5). The opposite trend observed for BdL (Fig. 5) supports mixing with low-temperature shallow gases. Differently, no variation in the composition of aromatics was found in TCM (Fig. 5): presumably the low temperature characterising the overall geogenic system and the lack of aromatic degrader microbes caused by the low amounts of aromatics (Fig. 2)

preserved alkylated-benzenes. Despite the relatively low reactivity of benzene, its degradation has been reported under both anaerobic and, to a higher extent, aerobic conditions, proceeding through the formation of phenol as an intermediate metabolite (Jindrová et al., 2002). We observed a relative enrichment of phenol on benzene only at SdN and CdM (from deep to shallow soil gases)

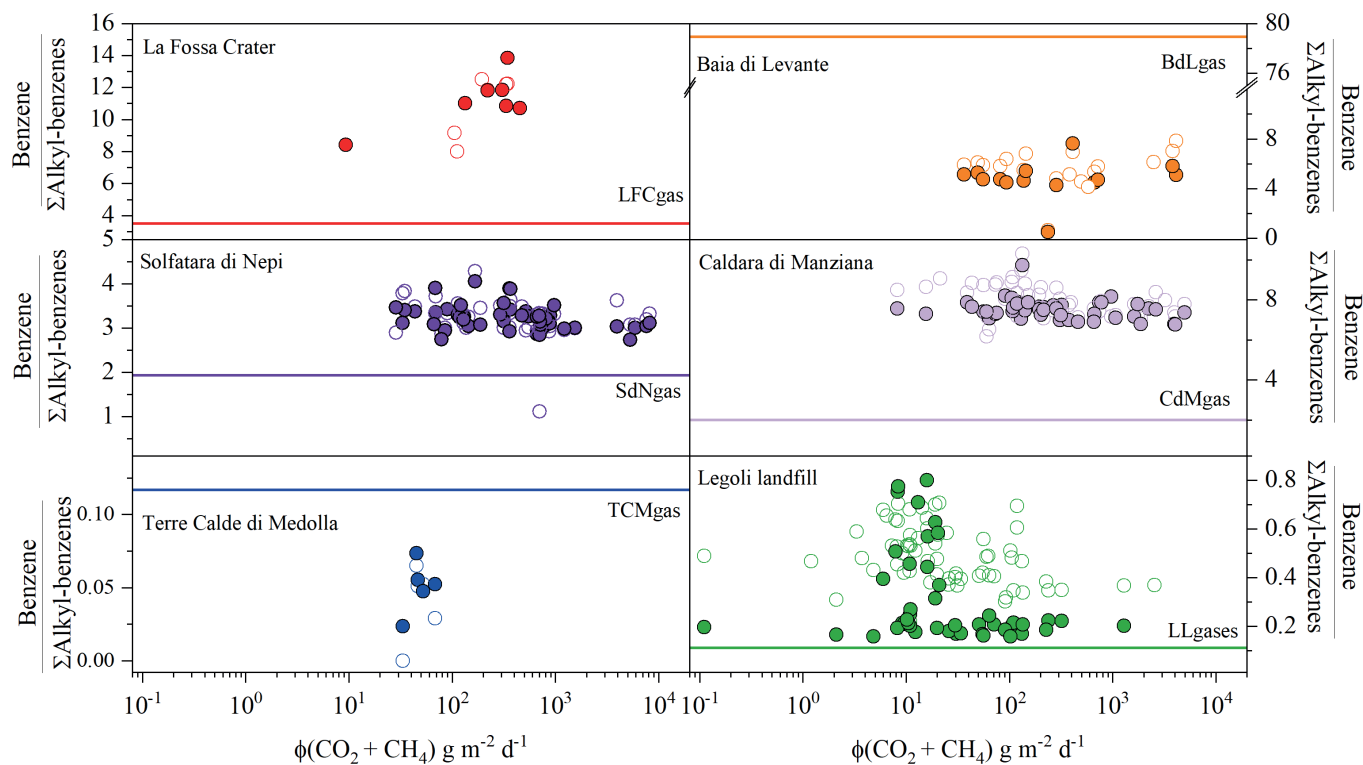


Figure 5 Binary diagrams of the ratios of benzene on alkylated benzenes (Σ Alkyl-benzenes) in soil gases. The Benzene/ Σ Alkyl-benzenes ratios of the source gases are also reported (bold lines). Solid and open symbols represent deep and shallow soil gas samples, respectively

and at BdL, LFC, and TCM where most soil gases were enriched in phenol with respect to benzene compared to the source gases. It likely reflected the development of phenol-degrading bacteria at variable depth.

Among S-substituted compounds, dimethylsulfoxide and dimethylsulfide were found in every investigated system except at TCM (Fig. 2), being their origin related either to high S fugacity (as occurred in volcanic/hydrothermal systems) or to degrading organic matter enriched in S (as occurred in MW landfill). The relative enrichment of dimethylsulfoxide on dimethylsulfide observed in the shallow soil gases with respect to deep soil gases and source gases confirmed the high reactivity of dimethylsulfide under oxidising conditions (Schäfer et al., 2010). Thiophenes were instead found only in volcanic/hydrothermal systems since their genetic environment is strictly related to reducing conditions, relatively high fS , and high temperature (Tassi et al., 2010). Given their strong similarity with the chemical structure of aromatics, cometabolic degradation of thiophenes with aromatics as a primary substrate has been reported (Joule, 2014). Actually, our data showed a relative depletion of thiophenes on alkylated aromatic compounds, suggesting that thiophenes were relatively more reactive.

Furans are typical high-temperature O-bearing organic compounds (Tassi et al., 2010) and were only detected at LFC and BdL (Fig. 2). Our data showed that furan is relatively less reactive than its methylated counterparts, which may support the lower stability of alkylated compounds with respect to the non-alkylated ones.

Terpenes occurred in relatively high amounts in LL soil

gases (Fig. 2) where they originate from the degradation of organic waste or direct volatilisation from detergents and air fresheners (Randazzo et al., 2020). Among these terpenes, we observed a relative increase of the concentration of α -pinene with respect to that, as a sum, of limonene and camphene upwards from the landfill gas to the shallowest gas samples, indicating a certain recalcitrance of α -pinene under oxidising conditions compared to its homologies.

No insight was observed into the degradation of neither halogenated nor N-substituted (benzothiazole) compounds.

Concluding remarks

Soil processes caused strong modifications to the compositional features of hypogenic gases affecting preferentially selected VOCs. The rates and types of these processes were different among the investigated systems, indicating a certain control of the soil conditions (e.g., microbial populations, organic matter and moisture contents, texture, structure, pH) and hypogenic gas composition.

The $\Phi(CO_2 + CH_4)$ values measured at the surface were not a reliable proxy for the residence time of the gas within the soil due to soil inhomogeneities.

O_2 availability appears to be a major control for the biogeochemical processes of selected VOCs, such as alkanes and dimethylsulfide.

LABORATORY EXPERIMENTS

Generation of VOCs from the anaerobic degradation of green waste

This experiment was focused on characterising the composition of VOCs originating from the anaerobic digestion (AD) of green waste (GW), as a representative category of the organic fraction of MW, with the scopes of (i) identifying the source processes and (ii) assessing its potential impacts if released into the atmosphere.

The experiment consisted of an AD reaction line, lasting about 50 days, at mesophilic conditions. The digester was filled with a mixture of GW with inoculum. GW consisted of municipal and domestic vegetal wastes, whilst the inoculum was an anaerobic sludge originating from municipal wastewater treatments. A total of 8 gases were periodically collected from the digester headspace. Semiquantitative VOC (C₄₊) analyses distinguished up to 29 different species in the GW biogases that were largely dominated by the high odorous terpenes in concentration, followed by alkanes and alkenes. These compounds are commonly synthesized by plants (Randazzo et al., 2022). Aromatic, halogenated, and S- and O-substituted compounds were found in lower amounts. Aromatics are also contained in vegetal tissues, such as lignin but they, together with halogenated compounds may be also assimilated by plants from contaminated air and soils (Randazzo et al., 2022). Finally, S- and O-substituted compounds are normally released by the degradation of fresh waste and decomposition of organic waste containing sulfur (Randazzo et al., 2022).

These results showed that GW, if disposed of in MW landfill, may potentially contribute to the overall odorous charge of MW biogas, releasing large quantities of terpenes.

Lab-scale prototype for simulating landfill cover soil

The second experiment was devoted to investigating the biochemical mechanisms by which landfill cover soils mitigate the complex variety of VOCs commonly pertaining to the landfill gas under controlled conditions. An experimental apparatus was properly designed and constructed to reliably simulate MW landfill systems. The apparatus consisted of a 20 L tank (digester), where the anaerobic digestion of selected waste categories (food

waste was selected as a representative category of the organic fraction of MW) occurred, connected to a vertical pipe (H = 60 cm, d = 15 cm) packed with vegetal soil (soil column). The generated biogas naturally flew from the digester into the soil column through pressure and concentration gradients. The experiment lasted for 23 days. Gases from the digester headspace and at regular intervals along the soil column were periodically collected and analysed in terms of: (i) main components i.e., CH₄, CO₂, H₂, N₂, O₂, and Ar; (ii) VOCs; (iii) δ¹³C-CO₂ and δ¹³C-CH₄. Overall, the concentration of biogas-related components (CH₄, CO₂, H₂, and VOCs) in the digester headspace and the soil column, sharply increasing in the first part of the AD, was relatively high until day 17 and then decreased. This decrease was associated with a drop in the N₂/O₂ ratios, indicating that air entered the digester i.e., biogas pressure was no longer capable of effectively counteracting air permeation along the cover soil. Along the soil column, the concentration of the biogas-related components relatively decreased upwards, mainly due to the air dilution effect. In the soil column, CO₂ and CH₄ always showed a ¹³C-enrichment compared to the corresponding source gases, according to the preference of microorganisms to metabolise the lightest isotope (Randazzo et al., 2020). We observed an increase of both O-substituted compounds and short-chain alkanes (C₂-C₃) on alkanes and long-chain alkanes (C₃₊), respectively, towards the top of the soil column, confirming the relative degradation of alkanes under aerobic conditions and the preferential degradation of long-chain alkanes compared to the short-chain ones. Consistently with the relative recalcitrance of benzene, a relative enrichment of benzene compared to alkylated-benzenes upwards the soil column was observed.

These results, consistent with the fieldwork observations, indicates that degradation processes occurring in landfill cover soils are highly selective for VOC compounds.

CONCLUSIONS

Soil processes caused strong modifications to the VOC compositional features of hypogenic gases during their uprising towards the atmosphere, especially pas-

VOCs relatively MORE affected by soil processes	VOCs relatively LESS affected by soil processes	VOCs as BY-PRODUCTS of VOC degradation pathways
Long-chain alkanes	Short-chain alkanes	O-Substituted compounds (aldehydes, esters, ketones, and alcohols) Phenol
Alkenes	Hexane	
Cyclics	Benzene	
Alkylated-benzenes	Phenol	
Dimethylsulfide	Dimethylsulfoxide	
Thiophenes	Furan	
Methylated-furans	α-pinene	
Limonene, Camphene		

Table 1 VOC species and groups classified on the basis of their behaviour in soil

sing within the soil where the physical-chemical conditions strongly differ respect to those dominating at the gas source. As shown in Table 1, the most reactive VOC species and organic groups in soil were recognised. Generally, long-chain and high-molecular weight molecules of alkane, alkene, cyclic, aromatic, and furan compounds were found to be relatively more affected by soil degradation processes. On the other hand, short-chain, low-molecular weight, and O-containing molecules were found to be recalcitrant to degradation processes with respect to their respective homologues (Table 1). Molecules characterised by six carbon atoms were among the less reactive compounds, confirming the relatively high chemical stability of the C₆ molecular structure. O-substituted organic compounds (i.e., aldehydes, esters, ketones, alcohols, and phenol), may be considered as tracers of the ongoing degradation of the VOCs, being them metabolites of hydrocarbon biodegradation pathways (Table 1).

Further investigation based on multidisciplinary approaches, involving microbiological, ecological, and pedological analysis, could provide new insights into the dependence of VOC degradation processes on soil microbial communities and micro-heterogeneities.

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