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BIOSPHERE-ATMOSPHERE EXCHANGE OF VOLATILE ORGANIC COMPOUNDS (VOCs) IN THE MEDITERRANEAN AREA

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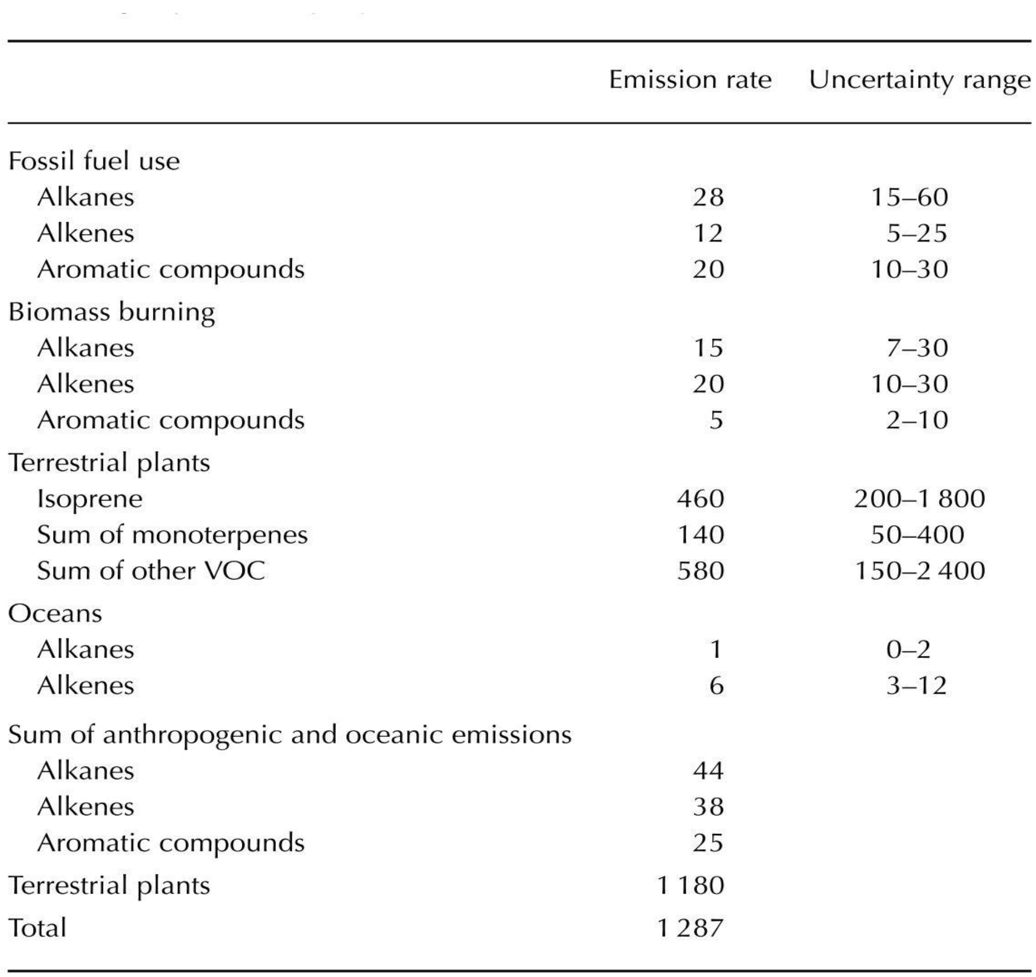
Table of contents

1. Introduction

1.1. What are Volatile Organic Compounds (VOCs): chemistry, sources and synthesis

The atmosphere is a mixture of gases, among which, tens of thousands of organic compounds present at mixing ratios of some 10 parts per billion (ppbv, 10^{-9} or nmol/mol) down to some parts per trillion (ppt, 10^{-12} or pmol/mol). All these different organic compounds comprising hydrocarbons, oxygenated species (alcohols, carbonyls, acids) and compounds containing heteroatoms (nitrogen or sulphur), are generally referred as 'volatile organic compounds' (VOC). Despite VOCs belong to different chemical species, they all have a vapour pressure greater than 10 Pa at 25 °C, a low boiling point at atmospheric pressure and 15 or less carbon atoms. A great number of processes on the earth result in the emission of VOCs (Fraser et al., 1998; Fortmann et al., 1998; Fall et al., 1999; McDonald et al., 2003; Barker et al., 2006). A portion of these emissions is due to anthropogenic activities (industrial fumes, car's exhaust gas, painting house, cooking and heating, making fire, waste management) and these VOCs are called anthropogenic volatile organic compounds (AVOCs). In addition, the earth's surface, including vegetation, soil and oceans, releases huge amounts of VOCs more specifically known as biogenic volatile organic compounds (BVOCs; Kesselmeier and Staudt, 1999). A list of VOCs released from several sources and their emission rates are summarized in Table 1. Nevertheless, the distinction between AVOCs and BVOCs is not always clear because many VOCs may be released by both biogenic-and anthropogenic sources; i.e. emissions of alkanes and alkenes are mainly released by anthropogenic sources, although can be also emitted by soil, ocean and wetland (Jacob et al. 2002). Even some oxygenated volatile organic compounds (OVOCs), like acetone and methanol, which are mainly emitted by vegetation (Goldstein and Schade 2000; Singh et al., 2004) can be also emitted from fossil fuel and biofuel combustion (Solberg et al.,1996).



	Emission rate	Uncertainty range
Fossil fuel use		
Alkanes	28	15–60
Alkenes	12	5–25
Aromatic compounds	20	10–30
Biomass burning		
Alkanes	15	7–30
Alkenes	20	10–30
Aromatic compounds	5	2–10
Terrestrial plants		
Isoprene	460	200–1 800
Sum of monoterpenes	140	50–400
Sum of other VOC	580	150–2 400
Oceans		
Alkanes	1	0–2
Alkenes	6	3–12
Sum of anthropogenic and oceanic emissions		
Alkanes	44	
Alkenes	38	
Aromatic compounds	25	
Terrestrial plants	1 180	
Total	1 287	

Table 1. VOCs sources and global annual emission rates (by Koppmann et al., 2007).

1.1.1. Anthropogenic VOCs (AVOCs) emissions to the atmosphere

The major anthropogenic contribute to VOCs emissions in atmosphere is related to fossil fuels (coil, oil and gas) exploitation. Approximately 100 Tg C yr^{-1} are estimated to be emitted from ‘technological’ sources and 150 Tg C yr^{-1} from all anthropogenic sources including biomass burning (Müller 1992). Coal production mainly leads to methane release, but minor emissions of ethane and propane are also present. Liquid fossil fuel production, storage and distribution result in a larger variety of VOCs emissions to the atmosphere. Crude oil production platforms are strong point sources of hydrocarbons such as methane, ethane, propane, butanes, pentanes, hexanes, heptanes, octanes and cycloparaffins (McInnes 1996). Combustion of fossil fuels produces mainly carbon dioxide and water, but also carbon monoxide (CO) and VOCs as by-products. The prevail emissions for gasoline and diesel combustion engines are paraffins (C1−−C5 for gasoline cars and methane for diesel engines), C2−−C5 olefins, ethyne, aromatic hydrocarbons (BTEX and C9 aromatics), aldehydes (formaldehyde, acetaldehyde, acrolein, benzaldehyde, tolualdehyde), ketones (acetone) and others (mainly high molecular weight paraffins). A further strong source of anthropogenic VOCs emissions comes from biomass burning (Lobert et al., 1990, Levine, 2003). However, anthropogenic VOCs may be emitted by other sources that are not yet well characterized, like landfill biogas.

Landfill gases are naturally generated by biological waste decomposition and they are mainly methane (∼50-60%), carbon dioxide (∼40%), and small quantities of VOCs (∼1–2%; Figure 1) (Zou et al., 2003; Themelis and Ulloa, 2007). Quite recently, considerable attention has been paid to collection, analysis and characterization of airborne VOCs into landfill emissions, because these minor biogas components are among the major air pollutants due their malodorous (Davoli et al., 2003), hazardous properties and potential toxicity to human health (ATSDR - Agency for Toxic Substance and Disease Registry, 1997, 2000; Durmusoglu et al., 2010). More than 500 compounds have been identified analyzing landfill gases (Parker et al., 2002) and their nature and concentrations depend on the composition of deposited waste and on chemical and biological processes occurring in solid waste (Chiriac, 2004). VOCs from household waste can have two origins: from anaerobic or aerobic fermentation of waste (microbiological production), or from direct volatilization of substances as toxic waste in dispersed quantities. Depending on the type of fermentation, the main VOCs groups are aromatic or chlorinated hydrocarbons for aerobic fermentation and sulfur compounds for anaerobic fermentation (Christensen et al., 1996). Benzene and other aromatic compounds are in fact formed from biological waste decomposition together with butadiene, methanol, 2-methyl-furan, trichloroethene, p-cymene and acetone (Knox, 1990; Allen et al., 1997). Carbonyls, cyclic alkenes and sulfur containing compounds are the main responsible of unpleasant smell of the biogas released from the landfill (Keller, 1988; Kim et al., 2006; Komilis et al., 2004; Zou et al., 2003).

Previous studies indicate that in urban atmosphere, the aromatic compounds, especially ethylbenzene and xylene, are related to the emissions from gasoline vehicles and gas stations (Cohen et al., 1991; Baldasano et al., 1998). Nevertheless, the landfill emissions contribution to the current atmospheric VOCs concentration is one of the most important sources besides industrial and vehicle sources (Zou et al., 2003).

Moreover, landfill biogas emissions can increase the levels of carcinogenic benzene and exceed the limits in the air (5 μg m^{-3} for the annual average concentration) established for human health (EEA – European Environment Agency, 2008). Besides benzene, other aromatics (e.g. toluene, xylenes and styrene) are present in the landfill biogas and can affect human health, even if their toxicity is lower than that of benzene (ATSDR - Agency for Toxic Substance and Disease Registry, 2000; IPCS – International Programme on Chemical Safety, 1997). In addition, chlorinated-VOCs such as trichloroethene and tetrachloroethene (PCE) are potentially carcinogenic (ATSDR - Agency for Toxic Substances and Disease Registry, 1997; Haddad et al., 1999; Rusyn et al., 2014).

The landifll biogas composition of VOCs strongly depends upon the type of waste and the time it underwent biological degradation (Allen et al., 1997). For instance, monterpenes like *D*-limonene and α-pinene are usually quite abundant in the biogas of urban waste landfills (Müller et al., 2004; Statheropoulos et al., 2005) due to the presence of vegetables and residues of household cleaning products (Allen et al., 1997; Schwarzbauer et al., 2002; Slack et al., 2005). Besides eucalyptol, in urban waste landfills are also usually detected sulfur compounds, ethers of natural origin and trimethyl arsine (Pinel-Raffaitin et al., 2007). A very high relative content of alkanes (i.e. *n*-butane) in the biogas can be an indicator of a very advanced stage of biochemical waste degradation (Wu and Wang 2015), whereas high p-cymene content, originated from the microbial transformation of monoterpenes, can be taken as an indication of a prolonged anaerobic waste degradation (Davoli et al., 2003). Although responsible of the unpleasant smell of aged waste, p-cymene is not toxic in the vapor phase, but has a great potential of ozone production (Orzi et al., 2010). On the contrary, a high relative content of *D*-limonene in the landfill biogas is highly indicative of a limited biochemical waste aging (Termonia and Termonia, 1999). Additional information on the stage of waste degradation can be obtained by comparing the type and content of some chlorinated-VOCs (e.g. 1,1-dichloroethene, 1,2-

dichloroethene, trichloroethene, tetrachloroethene and 1,2-dichlorobenzene) present in the landfill biogas. These AVOCs are common constituents of the landfill biogas produced by urban waste, as they come from the disposal of solvents used as degreasers and cleaners in both indoor and industrial activities (Dincer et al., 2006; Guha et al., 2012). Moreover, is to be taken into account that VOCs concentration variations can occur from winter to summer in relation with temperature and moisture content, which are responsible of a rapid biological degradation of organic matter and the production of relatively large volumes of biogas within landfills (Chiriac et al., 2007; Zou et al., 2003).

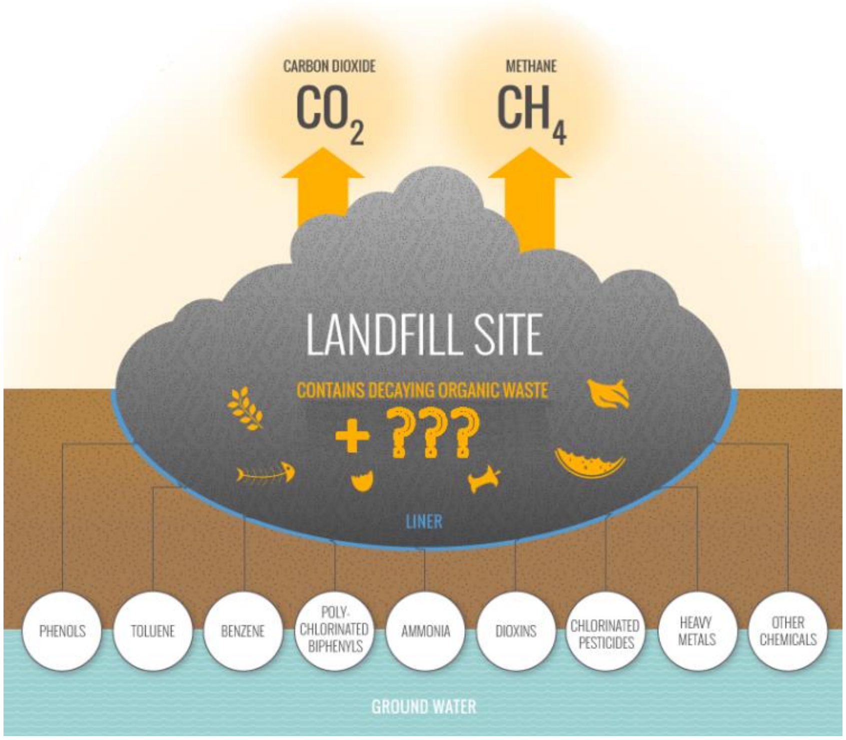


Figure 1. Biogas components generated by biological decomposition of landfill waste.

1.1.2. Biogenic VOCs (BVOCs) in the Earth system

Biogenic volatile organic compounds (BVOCs) emissions largely exceed anthropogenic sources (90% of total emissions) and are estimated to be ~760 Tg C yr^{-1}, especially from vegetative ecosystems (Sindelarova et al., 2014).

Many BVOCs have a constitutive production with emissions throughout the life cycle of the plant or at specific developmental stages (e.g. leaf and needle maturation, senescence, flowering). The emission can be biosynthetically controlled by abiotic factors such as light and/or temperature (Monson et al., 1992; Harley et al., 1996; Singsaas and Sharkey, 2000; Magel et al., 2007; Tiiva et al., 2007), atmospheric CO_2 concentration (Sharkey et al., 1991; Rosenstiel et al., 2003; Loreto et al., 1996; 2003; Rapparini et al., 2004; Wilkinson et al., 2009) and nutrition (Niinemets et al., 2010; Monson et al., 2013). Production of other BVOCs is induced after wounding (Davison et al., 2008; Brilli et al. 2012) feeding (Paré and Tumlinson, 1999; Frost et al., 2007; Brilli et al., 2009), or following environmental stresses (Loreto and Schnitzler, 2010). Stresses may induce change of constitutive BVOCs, either stimulating or quenching the emissions or inducing de novo synthesis and emission (Loreto et al., 2006).

The most emitted BVOC is isoprene (C_5H_8, 2-methyl-1,3-butadiene), followed by other isoprenoids and oxygenated-VOCs (i.e. methanol, acetaldehyde, acetone; Guenther at al., 1995). Isoprenoids are composed of C5 (or hemiterpene) building block structures, released from several types of vegetation species. These mainly include C10 compounds known as monoterpenes, C15 compounds as sesquiterpenes. Up to 5000 different isoprenoids structures have been identified in vegetation emission, of which 14 common (isoprene, limonene, α-pinene, p-cymene, etc.) species have been determined as dominant in BVOCs (Geron et al. 2000). Isoprene emission is light dependent and it is formed in the chloroplast from glyceraldehyde-3-phosphate and dimethylallyl diphosphate photosynthetic intemediates (Delwiche and Sharkey, 1993; Loreto 1996) through the methylerythritol phosphate (MEP) pathway (Lichtenthaler, 1999). Different to isoprene, monoterpenes (and sesquiterpenes) are usually stored in specialized structures and their emission is mainly controlled by physicochemical factors (Niinemets et al. 2004). Isoprene (C5) and monoterpenes (C10) are among the most studied BVOCs, because of their important role in the atmospheric chemistry (Fall 1999; Kesselmeier and Staudt 1999; Kreuzwieser et al. 1999; Lichtenthaler 1999). Monoterpenes have double bonds that can be contained inside a ring structure (endocyclic) or outside the ring structure (exocyclic), which position can affect their reactivity. Sesquiterpenes (C15 compounds) often contain several double bonds, leading to rapid oxidation after they are emitted to the atmosphere (Leaitch et al., 1999; Joutsensaari et al., 2005; Tholl et al., 2005). Emission of short-chained OVOCs (including methanol, ethanol, formaldehyde, acetaldehyde, formic acid, acetic acid and acetone) can be either constitutive or induced in many plants species (Guenther, 2002; Loreto 2006). Methanol is mostly emitted from leaves during degradation and formation of cell wall pectins occurring during cell expansion (Nemecek-Marshall et al., 1995; Fall and Benson, 1996), leaf abscission and senescence (Harriman et al., 1991) as well as during seed maturation (Obendorf et al., 1990). Methanol formation is catalyzed by pectin methylesterases (PME) which, among the other functions, demethoxylates pectin (Gaffe et al., 1994; Fall and Benson, 1996). With a smaller contribution, methanol can also originate from protein methyltransferase and protein repair reactions (Mudgett and Clarke, 1993), tetrahydrofolate metabolism (Cossins, 1987) and can be induced by mechanical wounding (Davison et al., 2008) or herbivore feeding (Penuelas et al., 2005; Korner et al., 2009), due to an upregulation of PME expression. Moreover, because its toxicity into the plants, methanol could be further metabolized to formaldehyde and formic acid (Oikawa and Lerdaus, 2013) both which, such as methanol, are partially emitted from leaves (Cossins, 1964). Formic acid, as well as acetic acid, can also originate from formaldehyde and acetaldehyde oxidation by OH-radicals (Bode et al., 1997; Kesselmeier et al., 1997).

Acetaldehyde is predominantly induced by environmental stresses and its emissions correlates with root flooding (Holzinger et al., 2000; Kreuzwieser et al., 2001) and with increased xylem sap ethanol concentrations (Kreuzwieser et al., 2002; Cojocariu et al., 2004). Roots ethanol production under anoxic condition promotes transport to the leaves through the transpiration stream, where ethanol is oxidized to acetaldehyde by alcohol dehydrogenase (ADH). However, only a small portion of acetaldehyde is emitted because is further metabolized by aldehyde dehydrogenase (ALDH) to acetate and acetyl-CoA (Kreuzwieser et al., 2001; Seco et al., 2007; Niinemets et al., 2014). A strong and transient bursts of acetaldehyde during light-to-dark transitions was observed in some trees species (Holzinger et al., 2000; Karl et al., 2002; Graus et al., 2004; Brilli et al. 2011), most likely as a result of a ‘pyruvate overflow mechanism’ where pyruvate decarboxylase (PDC) converts the excess cytosolic pyruvate into acetaldehyde, which is subsequently oxidized to acetate (Karl et al., 2002). Wounding and damaging events induce emissions of C6 aldehydes and alchols, collectively colled green leaf volatiles (GLVs) or LOX-products (Hatanaka, 1993; Fall et al., 1999; Laothawornkitkul et al., 2008). GLVs derive from the oxidation of polyenoic fatty acids, catalyzed by lipoxygenases (LOX). LOX start the octadecanoic pathway adding O_2 to unsaturated fatty acids generating 13-(S)-hydroperoxides. Afterward, 13-(S)-hydroperoxide lyase (HPL) catalyzes splitting of C12 and C13 releasing n-hexanal (from linoleic acid) and cis-3-hexenal (from a-linolenic acid) which are precursors for all other aldehydes and alcohols, and enzymatically acetylated compounds such as hexyl acetate and cis-3-hexenyl acetate (Croft et al., 1993; Feussner and Wasternack, 2002; Frost et al., 2007). Biosynthesis of the listed BVOCs are summarized in Figure 2. Other biotic and abiotic stresses can induce the emission of BVOCs such as methyl jasmonate (MeJA) and methyl salicylate (MeSA) from leaves (Takabayashi et al., 1994; Seo et al., 2001; Mithofer et al., 2005; Laothawornkitkul et al., 2008). Nowadays is well known that BVOCs have an important physiological and ecological role. In fact, BVOCs can protect plants against biotic and abiotic stresses. BVOCs can protect plants from pathogens by exerting an antimicrobial or antifungal activity (Croft et al., 1993; Shiojiri et al., 2006), or BVCOs can directly affect the physiology and the behavior of herbivores through their toxic, repellent and deterrent properties (De Moraes et al., 2001; Vancanneyt et al., 2001; Aharoni et al., 2003; Laothawornkitkul et al., 2008). In fact, leaves can be induced by herbivore to emit a blend of BVOCs that can attract insect or predators of the herbivore, in a tritrophic interaction (Karban and Baldwin, 1997; Mumm and Dicke, 2010). Moreover, GLVs (Engelberth et al., 2004; Farag et al., 2005) and isoprenoids (Arimura et al., 2002) can serve as airborne signals to activate mechanisms of defense between organs within the same plant (Karban et al., 2006; Frost et al., 2007; Heil & Silva Bueno, 2007) and between different plants (Engelberth et al., 2004; Kessler et al., 2006; Ton et al., 2007) or to prime a subset of

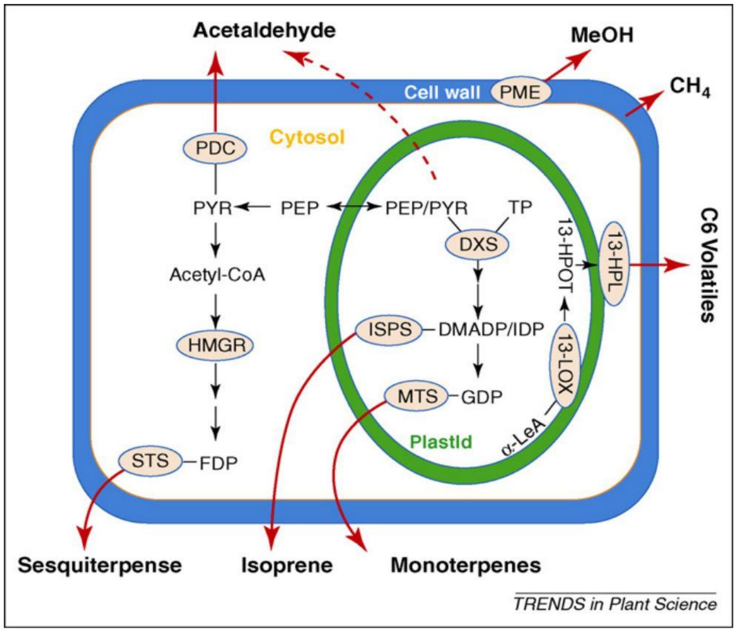


Figure 2. Simplified scheme of the subcellular biosynthesis of volatile organic compounds upon abiotic stress. CH4, methane; DMADP, dimethylallyl diphosphate; DXS, 1-deoxy-D-xylulose 5-phosphate synthase (EC 4.1.3.37); FDP, farnesyl diphosphate; GDP, geranyl diphosphate; HMGR, 3-hydroxy- 3-methylglutaryl-CoA reductase; 13-HPOT, 13S-hydroperoxy- 9(Z),11(E),15(Z)-octadecatrienoic acid; IDP, isopentenyl diphosphate; ISPS, isoprene synthase; α-LeA, a-linolenic acid; 13-LOX, 13-lipoxygenase; MeOH, methanol; MTS, monoterpene synthase; PDC, pyruvate decarboxylase; PEP, phosphoenolpyruvate; PME, pectine methylesterase; PYR, pyruvate; STS, sesquiterpene synthase; 13-HPL, 13-hydroxyperoxide lyase; TP, triose phosphate. (by Loreto and Schnitzler., 2010).

defense-related genes for earlier and/or stronger induction of a subsequent stress (Arimura et al., 2002). Moreover, is now known that isoprenoids can also act as antioxidants in leaves and confer protection against O_3-induced oxidative stress and singlet oxygen accumulation during photosynthesis (Loreto et al., 2001, 2004; Affek & Yakir, 2002; Vickers et al., 2009). However, concerning BVOCs interaction with abiotic and biotic ecosystem components, some important issues are still open and need particular attention. More specifically little is known about BVOCs exchanged by the soil, sources and sink, ecological and environmental emission driver as well as their key role in abiotic processes and biotic interactions. Some authors reported that soil BVOCs are involved in abiotic interactions among plant roots, fungi and bacteria (review, Wenke et al. 2010). The decomposition of soil organic matter by soil microorganisms is one of the most important abiotic process contributing to soil VOCs emissions (Leff & Fierer 2008). Moreover, soil can act also as sink, trough deposition of atmospheric VOCs (Schade & Goldstein 2001; Pegoraro et al. 2006; Asensio et al. 2007, 2008; Greenberg et al. 2012; Aaltonen et al. 2013) and the microbial consumption of VOCs as a carbon source (Misra et al. 1996; Cleveland & Yavitt 1998; Owen et al. 2007; Ramirez et al. 2009).

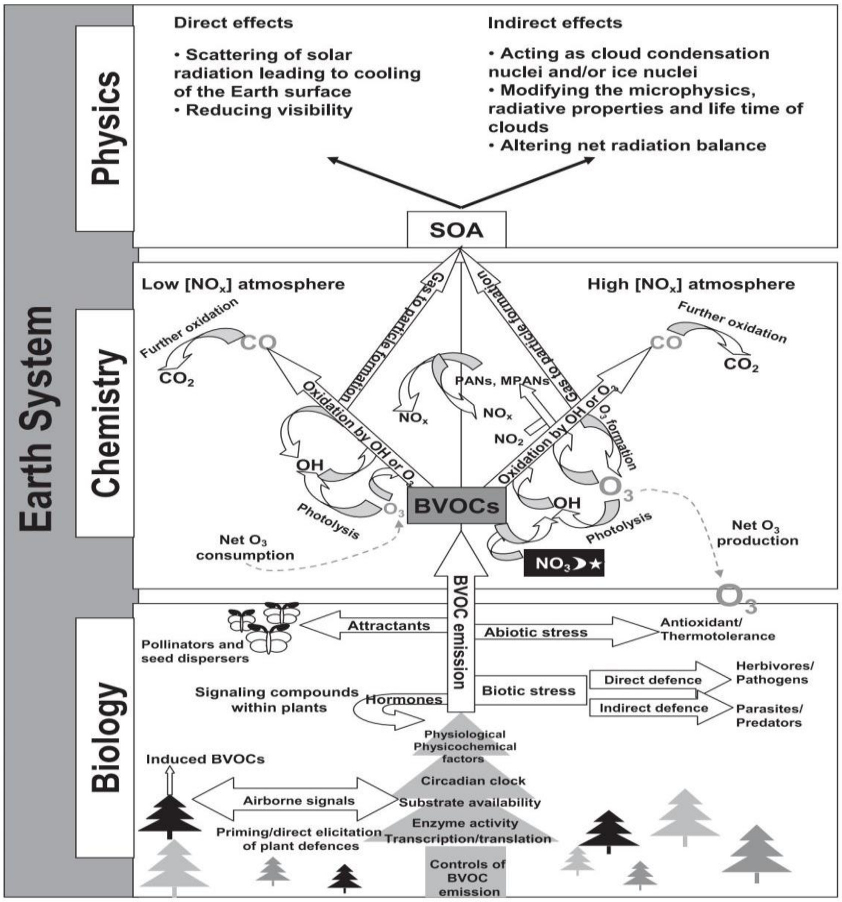


Figure 3. Schematic representation of the roles of biogenic volatile organic compounds (BVOCs) in the Earth’s ecosystems (by Laothawornkitkul et al., 2009)

1.1.3 BVOCs exchange from agricultural crops

Massive land use and land cover changes are occurring nowadays, not only as a result of climate change but also because of urbanization, agriculture and agro-industrialization These pressures may dramatically influence BVOCs emissions altering plants biome and species-specific characteristics (Laothawornkitkul, 2009). A global increase of 455% in crop area occurred in the past 300 years (Goldewijk, 2001). Nowadays agricultural areas cover around 35% of the Earth land surface (FAO, 2016). For several years, forests have been the most widely studied ecosystem concerning BVOCs emissions (Niinemets et al., 2013). Indeed, up to now, only few studies have measured BVOCs exchange in croplands (Warneke et al., 2002; Karl et al., 2005; Eller et al., 2011; Copeland et al., 2012; Crespo et al., 2013). In particular, in Europe, BVOCs emissions have been widely investigated only in short rotation coppices (SRC) of poplars (Ashworth et al., 2013; Brilli et al., 2016, Portillo-Estrada., 2018). Moreover, a number of studies focused only on maize, often providing measurements that spanned for short time periods during the early growth stages (Das et al., 2003; Graus et al., 2011; Leppik et al., 2014). Recently, only two studies monitored fluxes of BVOCs over an entire maize growing season and they mainly reported methanol, acetone, acetaldehyde, acetic acid, monoterpenes and GLVs fluxes (Bachy et al., 2016; Wiß et al., 2018). Previous research has documented that across Europe, by maintaining current genotypes, sowing dates, and the mix of rainfed and irrigated land use would result in a 20% decrease of maize yields by 2050 due to the climate change (Webber et al., 2018). Therefore, the assessment of BVOCs exchanged over the whole growing season in alternative, drought and heat resistant crops is needed. Grain sorghum (*Sorghum bicolor L.)* is a forage species and a valid alternative to maize for animal feed in Southern European regions, as well as in any non-irrigated area characterized by very limited precipitation, especially in summertime (Balole & Legwaila, 2006). Past laboratory experiments simulating leaf-drying/senescence have shown sorghum can be a source of acetaldehyde along with methanol and other oxygenated BVOCs (Karl et al., 2005).

1.2. VOCs impact on local air quality in the Mediterranean area

Regardless of the biogenic or anthropogenic source, once in the atmosphere VOCs are involved in many reactions playing an important role in atmospheric chemistry, affecting air quality and climate (Atkinson & Arey, 2003; Ashworth et al., 2012; Makkonen et al., 2012; Calfapietra et al., 2013; Schultz et al., 2015). In the atmosphere, reactive VOCs such as isoprenoids combine with hydroxyl radicals ($^{\bullet}OH$) and, in the presence of nitrogen oxides (NOx), peroxy radicals (RO_2) and high temperature intensities, can lead to the formation of O_3 and regeneration $^{\bullet}OH$ by photo-oxidation in under high light intensities (Fehsenfeld et al., 1992; Atkinson & Arey, 2003; 2012; Calfapietra et al., 2013). Then, VOCs oxidation can affect the troposphere oxidative capacity contributing to increase the greenhouse gases lifetime as methane (Atkinson & Arey, 2003; Lelieveld et al., 2008). This process can influence the Earth's radiation balance and the resulting climate changes can, in turn, directly and indirectly affect VOCs emission rates, establishing a positive feedback in the climate system (Wuebbles et al., 1989). Moreover, VOCs atmospheric oxidation and their oxidation products, in the presence of NOx, can lead to the formation of organic nitrates like peroxyacetylnitrates (PANs) and peroxymethacrylic nitric anhydrides (MPANs). These organic nitrates have longer atmospheric lifetime than NOx (days to months) and then can be transported over longer distances, acting as carriers of reactive nitrogen (Fehsenfeld et al., 1992). In addition, VOCs can also lead to secondary organic aerosols (SOAs) formation, because of their oxidation products that have lower vapour pressure and then can condense quickly on pre-existing molecular clusters (Joutsensaari et al., 2005).

Mediterranean ecosystems represent ~2% of the Earth's land surface. The environmental conditions of the Mediterranean area are peculiar and characterized by hot and dry summers, mild and often rainy winters, recurrent exposure to salinity due to sea breeze and saline ground water table, and sandy soil with poor organic fraction and nutrients (Joffre and Rambal., 2002). Because of these environmental constrains, despite the large biodiversity of the Mediterranean vegetation, all plant species display similar ecological adaptations. The morphological and structural adaptations to drought, salinity and high temperatures observed in the Mediterranean species involve small plant size, globular shape of the canopy and sclerophytic leaves with thick cuticles and dense mesophyll (Thompson, 2005). Few plants species developed a “water spending strategy” with stomata insensitive to water availability that allow high rates of photosynthesis only when water is available (Brilli et al. 2011). Most plant species present a “water saving strategy”, able to modulate stomatal and permanently restricted by anatomical, morphological and physiological traits, and low rates of carbon assimilation even in the absence of environmental constraints (Larcher, 2001). Emissions of isoprenoids and OVOCs are common among the plant species of Mediterranean ecosystems (Vickers et al., 2009). The impact of VOCs is expected to be more evident when biogenic and anthropogenic compounds are likely to react with pollutants. In fact, when the sea breeze switches into land system during the night, VOCs can react with primary and secondary pollutants in the air mass. Some of them, such as monoterpenes or sesquitepenes emitted with a temperature-dependent mechanism, can act as a nighttime sink of ozone reacting with it and leading to carbonyl and radical formation (Ciccioli and Mannozzi, 2007).

In light of these characteristics, Mediterranean area is a sensitive region affected by both particulate and gaseous pollutants. In fact this climatic region there is a combination of polluted air masses transported over long distances and from three continents (Europe, Asia and Africa – e.g., Lelieveld et al., 2002; Pace et al., 2006) with local anthropogenic emissions, natural emissions (Kalogridis et al., 2014; Owen et al., 2001) and forest fires (Bougiatioti et al., 2014). Consequently, particulate and O_3 concentrations are higher in the Mediterranean region than in most continental European region especially during summertime (Doche et al., 2014; Menut et al., 2015; Nabat et al., 2013; Safieddine et al., 2014), since climatic conditions favor the development of photochemical processes (Fountoukis et al., 2011). Moreover, the Mediterranean is also regarded as a notorious climate change “hot spot” which is predicted to undergo significant warming and drying in the 21st century (Giorgi, 2006; Kopf, 2010; Lelieveld et al., 2014). As we know, both reactive AVOCs and BVOCs are key players in photochemical processes leading to secondary pollutant formation (Seinfeld and Pandis, 1998; Goldstein and Galbally, 2007; Seco et al., 2007). These compounds can react with atmospheric oxidants leading to increasingly functionalized products with sufficiently low volatility (Aumont et al., 2012; Jimenez et al., 2009; Kroll and Seinfeld, 2008) taking part in the formation of SOAs by nucleation or condensation onto preexisting particles (Fuzzi et al., 2006; Kanakidou et al., 2005). Moreover, in the Mediterranean region, OVOCs can derive from primary sources, mainly biogenic emissions, and secondary sources like the oxidation of anthropogenic and biogenic hydrocarbons (Debevec, 2017). The latter source makes more difficult to assess their origins directly and contributes considerably to their abundance at rural and remote sites because of the atmospheric transport (Solberg et al. 1996; Goldstein and Schade 2000; Singh et al. 2004). Focusing the attention on BVOCs and their driving factors in the Mediterranean area, isoprenoids are the major primary compounds (Debevec, 2018). Monoterpenes follow a nighttime pattern related to nocturnal emission from monoterpenes-stroring plants, whereas isoprene shows a daily pattern related to temperature and radiation (Figure 4). OVOCs mixing ratios in the Mediterranean area depend on long-distance transport and biomass burning (Salisbury et al., 2003; Holzinger et al., 2005).

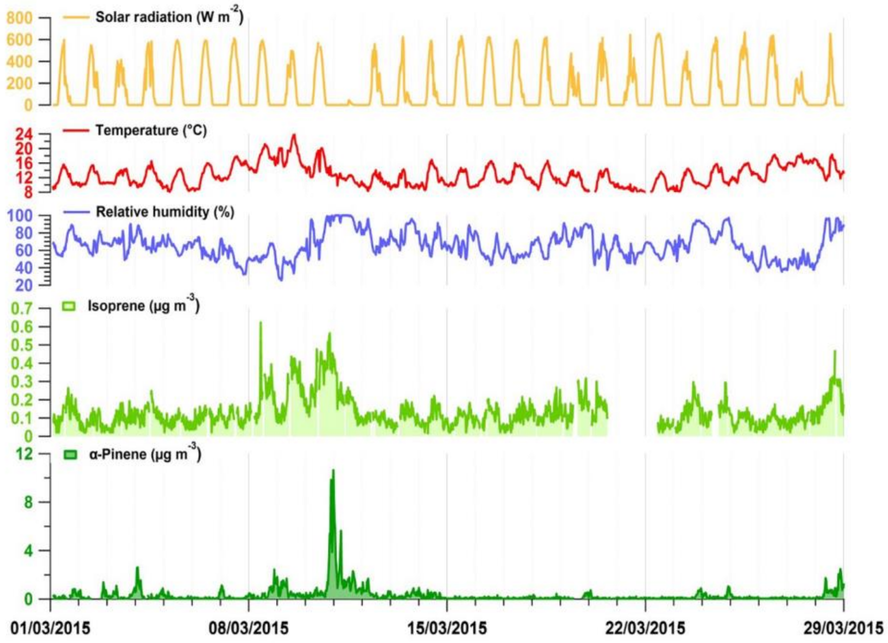


Figure 4. Time series of isoprene and α-pinene in comparison with meteorological parameters (solar radiation, temperature and relative humidity) in a Mediterranean background site (Cyprus) (from Devebec et al, 2017).

1.3. Objectives

This PhD thesis aims at: determine the AVOCs composition and emissions rate from an illegally managed waste landfills (1st study case); measure the BVOCs fluxes, at ecosystem-scale and for the whole growing season, above a sorghum crop cultivated in Southern Europe (2nd study case).

In particular, the objectives of this PhD thesis include:

(i) characterization of the chemical composition and concentrations of AVOCs emitted in the atmosphere from a still poorly investigated anthropic source such a landfill located in Southern Italy;

(ii) measure the exchange of BVOCs from an agricultural ecosystem located in the Mediterranean area for the whole growing season;

(iii) explore the possibility of using BVOCs fluxes to characterize the different growth stages of sorghum and to track the occurrence of stressful events (i.e. lodging and cuttings).

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2. Materials and Methods

2.1. VOCs analysis and flux measurements techniques

2.1.1. Sampling by cartridges and analysis by Thermo-Desorption Gas Chromatography Mass Spectrometry (TD-GC-MS)

Gas chromatography coupled with electro impact mass spectrometry (GC-EIMS) dominated the past 30–40 years of research on VOCs (Darley et al. 1963; Ciccioli et al., 1993; Helmig 1999; Ciccioli et al., 2002). In gas chromatography (GC) the mobile phase, a highly diffuse gas, is used to solvate and transport components within a mixture through or over a stationary phase, with separation occurring due to differences in the rates of migration (Figure 1). The mobile phase must have a high diffusion coefficient to ensure maximum numbers of gas–stationary phase interactions. Highest separation efficiencies are achieved using hydrogen, which have a wider linear velocity range than helium.

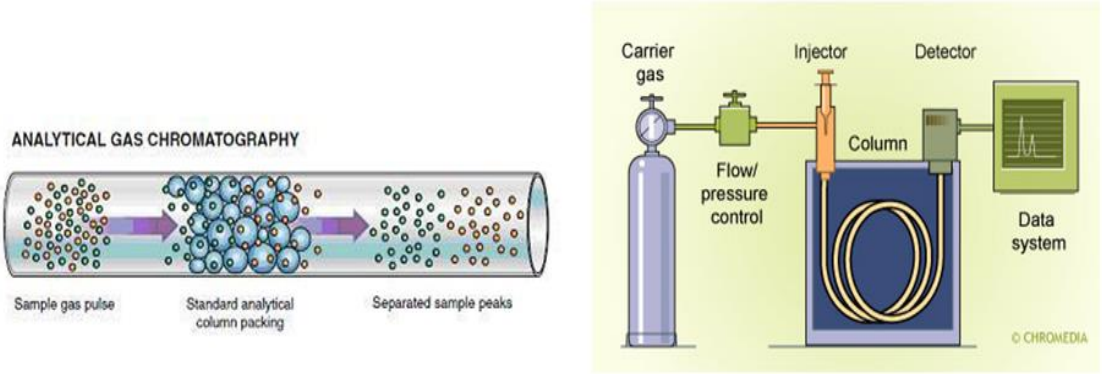

Figure 1. Schematic representation of mobile phase-stationary phase interaction into chromatographic column and gas chromatography system.

The time a compound takes to be eluted from the column is known as the retention time and is used as a criteria for the identification of VOCs. In a correctly optimized chromatographic separation the analyte band will reach the detector in a narrow plug with a degree of band broadening to produce a Gaussian-shaped peak. The area under the peak is representative of the sample concentration giving a quantitative measurement. Storing of atmospheric samples is a critical factor as to whether analysis may be performed back in the laboratory or on-site immediately following acquisition. In fact, samples can be either introduced directly into the instrument in the field or collected in pressurized steel canisters, absorbent packed cartridges or filters for later analysis in the laboratory. A widely used method of collecting air samples is based on the use of a solid phase adsorbent (which is a very high capacity packed column) as trap. The adsorbent used in these trap may be chosen introducing an element of selectivity to the trapping mechanism, although in practice a “trap-all” approach is commonly used. A huge range of adsorbent supports are commercially available (Camel and Caude 1995), ranging from high surface area (>1000 m^3/g) carbon material (both charcoals and graphitized) with strong retention characteristics, to lower surface area (<50 m^3/g) polymeric such as Tenax TA. Samples may be introduced to the adsorbent tubes either over short periods of time (typically minutes) or via diffusional sampling over longer periods (typically several days). Carbon-based adsorbents are suitable for a wide range of species ranging from volatile hydrocarbons and CFCs to organic nitrates. Polymeric materials are used mainly for the concentration of lower volatile species such as aromatics and monoterpenes, although compounds as large as 2- and 3-ring polycyclic aromatic species may also be successfully trapped and thermally or solvent desorbed. Compounds quantification is allowed using an external standard calibration approach, employing a calibrated VOCs gas cylinder containing known concentrations of different VOCs and liquid mixture of VOCs solutions which are diluted at five concentration levels. Blank emissions and artifact formation, which can affect method sensitivity and overall performance, were determined using clean tubes.

2.1.2. Real-time measurements: Proton Transfer Reaction Time-of-Flight (PTR-TOF)

The recently developed proton transfer reaction quadrupole mass spectrometry (PTR-QMS) is a combination of a PTR drift tube and a quadrupole mass spectrometer (MS), which allows fast and continuous detection of VOCs in air sample without the need of any pre-concentration stage (Hansel et al., 1995; Lindinger et al. 1998). PTR-QMS can detect VOCs concentration in air with a high sensitivity in the range of part per trillions (ppt). Consequently, PTR-QMS has found numerous applications in atmospheric chemistry, biology, and other scientific fields such as food technology and medicine (Lindinger et al. 1998; Critchley et al., 2004; Riess et al., 2010; Aprea et al., 2007; Mateus et al., 2007; Majchrzak et al, 2018). All forms of mass spectrometry depend dependent on the ionization of the molecular compounds. In order to achieve ionization avoiding excessive fragmentation, proton transfer reactions from protonated water can be used (Lindinger, 1993). An ion source (IS) generates H_3O^+ (hydronium) which is transferred to the drift tube of the PTR-MS. Then, hydronium is used as a proton donor (or primary ion) to the trace gas (R) measured (Equation 1).

$$H_3O^+ + \mathrm{R} \leftrightarrow \mathrm{R}H^+ + H_2O$$

Equation 1. Proton transfer reaction equation.

If the proton affinity (PA) of R is higher than the PA of water the equilibrium strongly shifts to the right-hand side of the proton transfer reaction and the steady state will almost entirely consist of the protonated compound and water. If a compound has a PA above but close to that of water (i.e formaldehyde), the exothermicity of the reverse reaction will be non-negligible. Water proton affinity is above that of the common atmospheric constituents. For these compounds, the equilibrium reaction shifts strongly to the left-hand side and any ionized molecule is rapidly converted back to primary ions and non-protonated compound. In the hollow cathode ion source, H_3O^+ reagent ions are produced from water vapor introduced as reagent gas from a liquid water sample holder. PTR-ion source is typically operated at E/N (E being the electric field strength in volts per centimeter, N being the number density in molecules per cubic centimeter, in the reaction cell) of 120 10^{-17} Vcm^2. Reagent ions are entering the adjacent drift tube section, where the sample to be analyzed is continuously injected (via a gas inlet system with adjustable flow between 50 and 1000sccm and adjustable temperature between 40 and 150 °C) with typical pressures maintained between 2.2 and 2.4 mbar. Drift tube and mass spectrometer are connected through chambers at different pressures and ions are guided through these chambers by electrical lenses. Since atmospheric samples may contain thousands of VOCs, PTR-MS mass spectra can be hard to interpret due to the large number of peaks and the lack of discrimination between isobaric compounds. In fact, one of the disadvantages of PTR-MS is the fact that only the nominal mass-to-charge ratio of the protonated parent ion can be determined preventing a unique identification of the VOCs. The presence of several different species on the same nominal mass, cluster ion and parent ion fragmentation may lead to complications in the interpretation of ion signals. Through the years, several approaches have been reported to improve the selectivity of the instrument, by combining the PTR-ionization with more powerful separation techniques. In the first decade of 2000s, several groups reported the coupling of a chemical ionization to a time-of-flight mass spectrometer (Blake et al., 2004; Ennis et al., 2005; Tanimoto et al., 2007; Wyche et al., 2007). Improvements comprise a higher mass resolving power (Blake et al., 2004) and detection limits in the 100 pptv range for 1 min integration time (Tanimoto et al., 2007). The increased mass resolution allows the separation of a limited number of isobaric VOCs that quadrupole PTR-MS cannot distinguish. However, detection limits are two orders of magnitude poorer compared with conventional PTR-MS. Jordan et al (2009) and Graus et al (2010) showed the first application of the commercially available PTR-TOF, which consists of a proton transfer reaction (PTR) ion source (Ionicon Analytik GmbH, Innsbruck, Austria) and an orthogonal acceleration, reflectron time-of-flight mass spectrometer (TOF-MS; Tofwerk AG, Thun, Switzerland) having a better mass resolution and a detection limit that is at least one order of magnitude

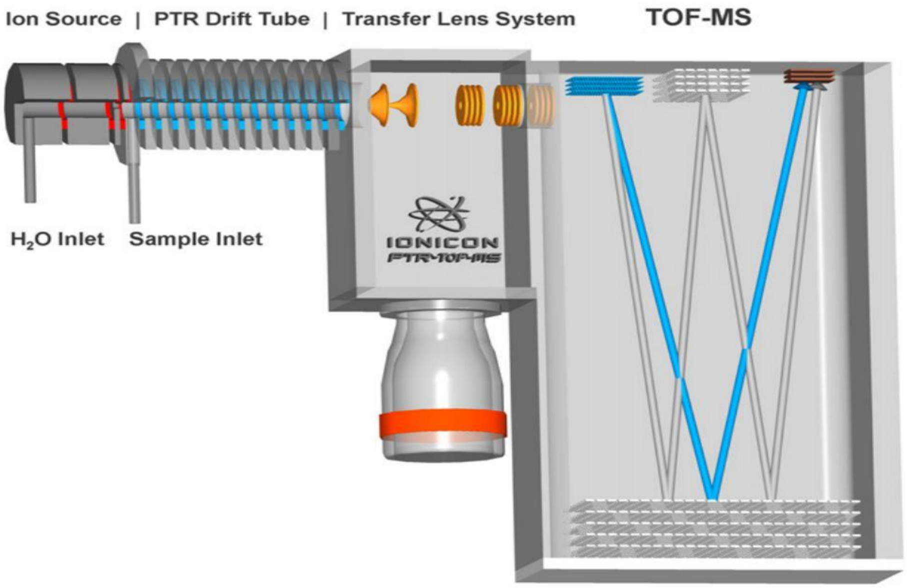

Figure 2. Scheme of the PTR-TOF-MS instrument, consisting of the hollow cathode discharge ion source, the drift tube reaction chamber, the transfer lens system and the reflectron time-of-flight mass spectrometer (Jordan et al., 2009).

lower than of those demonstrated in the literature (Blake et al., 2004; Blake et al., 2009). (Figure 2). The entire PTR-TOF-MS instrument is mounted in a single mobile rack, where the mass spectrometer, the ion source and drift tube system, the vacuum system (2 split-flow turbo pumps and 1 foreline backing pump) and the whole electronics including the pulse generator are all integrated. After the proton transfer reactions between hydronium ions and VOCs in the drift tube, the outgoing protonated VOCs ions then enter, via a specially designed transfer lens system, the pulse extraction region of the orthogonal acceleration reflectron time-of-flight mass spectrometer. Here ions are accelerated into the TOF section at a typical repetition rate of up to 80kHz. TOF-MS section must be operated at high vacuum ($<1 \times 10^{-6}$ mbar) to ensure a collision free passage of the ions through the flight tube. A differentially pumped ion transfer unit couples the PTR-ion source with the TOF-MS, allows for keeping up both pressure regimes, and maintains the sample flow through the drift. The interface for the PTR-ion source and the geometry of the ion extraction into the first differential pumping stage were optimized for ion transmission and thus sensitivity. The ion optics is a lens system that collimates the ions to a virtually parallel beam. At the end of the ion optics, the ions enter the pulser through an aperture. All ions are periodically extracted every 30 µs from the ion beam in orthogonal direction. After acceleration and passage through a field-free region, the ions are reversed in a reflector and thereby refocused in the detector plane where they are detected by multi-channel-plates (MCP; Burle Industries Inc., Lancaster, PA, USA). An amplifier discriminator (Ionwerks XCD; Ionwerks Inc., Houston, TX, USA) amplifies the MCP signal by a factor of 50 and triggers the input channel of the time-to-digital converter (TDC, 0.1 ns minimum bin width) if the signal exceeds the threshold level (typically 30–40 mV). Optimization of the MCP gain setting and threshold level allows for effective electronic noise suppression. This increases the signal-to-noise ratio and hence improves the limit of detection (LOD) of the PTR-TOF-MS. At the end, mass-to-charge ratios of the ions are determined from the flight times measured at each extraction pulse generating a complete mass spectrum for the chosen mass range. A data acquisition software controls the timing of the pulser and the TDC, acquires the raw data and stores series of mass spectra according to the chosen data structure in HDF5 format, together with meta-information on the data acquisition.

2.1.2.1 Instrumental background, calibration, sensitivity, concentration determination and limit of detection (LOD)

Assessment of the PTR-TOF-MS background is essential to ensure the accuracy of the data recorded. To measure the background, air sample analyzed by the PTR-TOF-MS must not contain any VOCs. I order to do that, the most popular method is the use of a catalytic converter to remove all the VOCs from the air while preserving the same level of humidity and oxygen content in air. The form, length and materials of a catalytic converter can vary considerably among the devices. Generally, VOC are removed from air by passing through the heating of quartz wool, platinum dust or activated carbons within the catalyst (Golunski, 2007). The background signal for a VOC is simply the count-per-second normalized to the intensity of the primary ion signal (H_3O^+) (ncps) recorded at the mass at which the compound is detected when an air sample first pass through the heated catalyst. At the end, the background cps is taken into account by further subtracting it from the same signal recorded form the air samples (de Gouw et al., 2007). Two approaches are usually used to calculate the volume mixing ratio (VMR) from the protonated ion signals recoded by PTR-TOF-MS which are related to VOCs and/fragment of VOCs. The 'calibration approach' (de Gouw et al., 2003, 2007) is based on direct measurements of a gas standard containing a well-known concentration of VOCs in order to estimate PTR-TOF-MS sensitivity for VOCs. Calculation of VMR is done dividing the ion signal recorded PTR-TOF-MS in sample air by the sensitivity (Equation 2).

$$VMR = \frac{ncps}{S}$$

Equation 2. Calculation of volume mixing ratio (VMR) by dividing normalized ion signal to sensitivity.

Following this method, the sensitivity of specific VOCs, which has been experimentally determined, is the coefficient used to convert ncps to a VMR. The unit of measurement of the VMR is commonly given in ncps/ppb. There are two main advantages for this experimental method to measure the PTR-TOF-MS sensitivity: better constrained accuracy and user friendliness. Indeed when measured, PTR-TOF-MS sensitivity for a specific VOC includes the mass dependent transmission efficiency, and automatically accounts for isotope peaks and possible fragmentation. However, this method is limited to the VOCs contained within the mixture of the gas standard used for calibration, and then only a few VOCs can be calibrated. The other 'theoretical' method to assess PTR-TOF-MS sensitivity and VMR of VOCs relies on a calculation based on the fundamental physical conditions of the proton transfer reaction occurring within the drift tube (pressure, length, E/N, ion mobility, etc.) via first order kinetic reaction (Lindinger et al., 1998), after applying the correction for the effect of the duty cycle (Cappellin et al., 2012, Equation 3):

$$[VOC]_{VMR} = \left(\frac{1}{k\tau}\right) \times \left(\frac{[VOCH^{+}]measured}{[H_3O^{+}]measured}\right) \times \left(\frac{\sqrt{\left(\frac{m}{z}\right) H_3O^{+}}}{\sqrt{\left(\frac{m}{z}\right) VOCH^{+}}}\right)$$

Equation 3. Theoretical absolute formula to calculate VOCs concentration via first order kinetics reaction and correction for the duty cycle (Cappellin et al., 2012).

where [VOC-H^{+}] and [H$_3$O^{+}] are signal ion rates corresponding to the protonated VOC and the primary ion, respectively; τ is the reaction time of [H$_3$O^{+}] in the drift tube (de Gouw et al., 2003; Tani et al., 2003); *k* is the reaction rate coefficient between VOC and H$_3$O^{+} according to the values provided by Cappellin et al. (2012). When *k* is not available, a standard value of $2*10^{-9}$ cm^3 s^{-1} is used. For a better accuracy, the [$H_3{}^{16}O^{+}$] concentration at m/z = 19.018 is calculated multiplying by 500, the signal of the natural isotope [$H_3{}^{18}O^{+}$] measured at m/z = 21.022. The great strength of this approach is the ability to calculate VMRs for any VOCs for which reaction rate coefficients can be estimated. Limit of detection (LOD) is determined by the minimum signal to noise ratio required to effectively quantify the VMRs of VOCs measured by PTR-TOF-MS. A value of three is commonly used and in this case the LOD is given by (Equation 4):

$$LOD = \frac{3}{\frac{signal}{noise}} \times VMR$$

Equation 4. Calculation of limit of detection (LOD) as three times large signal respect to the noise.

2.1.2.2. Data management, processing and analysis

After acquisition, PTR-TOF raw data are usually acquired and stored in HDF5 file format (http://www.hdfgroup.org/) and each file is post-processed through the PTR-TOF Data Analyzer software (Müller et al., 2013). This software performs a careful mass scale calibration and peak detection by peak shape analysis, iterative residual peak analysis for the multiple isobaric peaks detection per unit m/z, and fitted peak areas quantification corresponding to ion signal intensities based on the sum spectra. Calibration of the mass scale of all recorded spectra is made both by exploiting three well-defined PTR-TOF-MS background ion peaks (m/z=21.0221, m/z= 29.9974 and m/z= 39.0327 corresponding to $H_3O^{18+,}$ NO^+ and H_2O-$H_3O^{18+,}$ respectively), and diiodobenzene (m/z = 203.948) continuously inserted into the sample inlet. In order to prepare data to be use for computing eddy covariance fluxes, a single mass list is obtained by processing one or more raw HDF5 data files with the PTR-TOF Data Analyzer software. Subsequently, all the HDF5 files recorded in a day or in half of day time length are grouped a processed together by using the same mass list. The resulting daily files are post-processed by using a custom-made Matlab R2018b routine (The MathWorks Inc., Natick, MA, USA), where background average subtraction, fragments correction, theoretical concentration calculation and despiking were performed. Finally, processed data are stored and saved in half-hour text files for fluxes computation.

2.2. Eddy Covariance flux measurements

The Eddy Covariance (EC) allows measurements of gas fluxes representative of a surface area (footprint) ranging from a few hundred to millions of square meters. EC method is based the direct high frequency measurements of the gas concentration in air combined with the vertical component of the wind speed, resulting in calculations of turbulent fluxes within the atmospheric boundary layer. This method has been widely used in micrometeorology for over 30 years and recently has been applied to the measurements of VOCs fluxes from ecosystems (Rosenberg et al., 1983; Wesely et al., 1989; Lee et al., 2004; Foken, 2008). A flux can be defined as an amount of mass that moves through a surface per unit of time. If the flux moves away from the surface, the surface is called ‘source’ and the flux ‘emission’; on the opposite, if the flux moves to the surface, the surface is called ‘sink’ and the flux ‘deposition’. In nature, the air flow can be imagined as a horizontal stream of rotating eddies, whereas each eddy has 3-D components, included vertical movement of air. Conceptually, this is the framework for atmospheric eddy transport (Wyngaard, 1990; Kaimal and Finnigan, 1994; Foken, 2008). Focusing the attention at a single point and at given time t1, an eddy can move a parcel of air c1 downward with a wind speed s1; at next moment t2 an eddy can move a parcel of air c2 upward with a wind speed s2. Each parcel of air can has its own properties, such as concentration, temperature, humidity, etc. By measuring these properties of the air parcels and vertical speed of the air is possible to know the vertical upward or downward fluxes of gas concentration, temperature, humidity, etc. The principal concept of Eddy Covariance is ‘the covariance between the concentration of a scalar and eddies vertical wind speed’ (Baldocchi, 2005). A flux can be represented by the equation (Equation 5) for which a flux is equal to the mean product of air density, vertical wind speed and mixing ratio of the scalar:

$$F = \overline{\rho_{\alpha}\, w'c'}$$

Equation 5. General equation for vertical flux calculation in turbulent flow.

where ρ_α is the air density, *w'* the vertical wind speed and *c'* the mixing ratio of the scalar. Flux calculation by EC is based on the Navier-Stokes equations and on the Reynolds' postulates (Foken and Wichura, 1996). According to Burba and Anderson (2010) the major assumptions used in EC include: measurements in a point represent an upwind area; measurements are done inside the boundary layer of interest; fluxes are measured only on the area of interest (the footprint is correctly chosen); the flux is fully turbulent; the terrain is horizontal and uniform; the instruments are detecting very small changes at very high frequency. An important concept related to EC method is the footprint, which represents the area around the measurement point from which the measured values come from. The measurements do not represent the area just below the sensor, but an area upwind from the measurement point (Foken, 2008).

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Because of assumptions, physical phenomena, instrumental problems, specifics of the particular terrain or setup, EC calculation can lead to several potential errors, although they can be accounted and corrected. Errors in the estimation of the EC may concern the frequency response and include those due to instrumental time response, sensor separation, scalar path averaging, tube attenuation, high and low pass filtering, sensor response mismatch and digital sampling. Time response errors can also occur because instruments may not be fast enough to catch all the rapid changes of the eddy transport. Sensor separation error can due to physical separation between wind speed and concentration measurements, so covariance is calculated for parameters measured at different points. Path averaging error could due to the fact that the sensor path is not a measurement point, but rather integration over some distance. Tube attenuation error could be observed in closed-path analyzers, and it is caused by attenuation of the instantaneous fluctuation of the concentration in the sampling tube. There can also be frequency response errors caused by sensor response mismatch, or by filtering and digital sampling (Foken and Oncley, 1995; Moncrief et al., 1996; Fuehrer and Friehe, 2002). Combined, all these errors may sum to over one hundred percent of the initial measured flux value. To minimize such errors, a number of procedures exist within the Eddy Covariance technique. Frequency response errors can be partially remedied by proper experimental set up, and corrected by applying frequency response corrections during data processing. Time delay errors can affect all fluxes, but those are most severe in closed path systems with long intake tubes, especially for water vapor and other “sticky” gases like ammonia and some VOCs. Such errors can be fixed by adjusting the time delay during data processing. It is also possible to fix time delays errors by shifting the two time of concentration and vertical wind speed series in such a way that the covariance between them is maximized, or by computing a time delay from the known flow rate and tube diameter. In addition, spikes and noise may impair EC flux calculation, but a spike removal routine and filtering help to minimize such errors.

2.2.1. Computation of Eddy Covariance VOCs fluxes

To measure the VOCs exchange at ecosystem level, eddy covariance (EC) is the most used micrometeorological method employed for fluxes computation (Cao and Hewitt 1999). The EC method provide a broader picture of the VOCs fluxes emitted and deposited in a whole ecosystem, and can be deployed over longer timescales to observe the response of fluxes to changing environmental conditions. The first published measurements of BVOCs fluxes by using the EC method utilized a fast chemiluminescence sensor to measure isoprene fluxes (Guenther and Hill , 1998), and more recent studies have employed PTR-MS (Karl et al. 2001; Warneke et al. 2002; Rinne et al. 2002; Lee et al. 2005; Bamberger et al., 2010; Graus et al., 2013) and PTR-TOF-MS techniques (Müller et al., 2010; Ruuskanen et al., 2011; Park et al., 2013; Brilli et al., 2014; Bachy et al., 2016; Brilli et al., 2016; Portillo-Estrada., 2018). The two data streams of PTR-TOF-MS and 3-D sonic anemometer are acquired on two different PC devices, then all acquisition times are synchronized by using a NTP time server. Then VOC fluxes are computed by applying the EC method to both the signals recorded with PTR-TOF-MS at 10 Hz and the signals recorded with the sonic anemometer at 20 Hz. This routine computation of EC fluxes includes: a) three-axis coordinate rotation of the wind data based on McMillan (1988); b) re-sampling of the 20 Hz wind data to match the 10 Hz VOCs data; c) maximization of covariance analysis of VOCs concentrations and vertical wind velocity for time-lag analysis; d) calculation of the covariance (*F*) between the vertical wind speed and the VOCs concentrations. By using this routine, half-hourly mean flux values are generated.

2.2.2. Time lag determination, uncertainty and limit of detection (LOD) of the fluxes

The main sources of random uncertainties in EC measurements are related to the stochastic nature of turbulence sampling and to instrument noise and as well as to the resolution of recording system. Many studies have addressed the problem from the perspective of an analytical system with fast-response time series and with good signal-to-noise ratio (SNR) e.g. fluxes of sensible heat, CO_2 or H_2O, because for these measurements, the uncertainty in the flux is typically dominated by natural turbulence variability. When the EC method is applied to estimate fluxes of gases, difficulties arise to measure precisely at a rate sufficient to meet the requirements of the technique in case of VOCs (VOCs; Karl et al., 2002; Langford et al., 2010; Park et al., 2013), ozone (O_3; Coyle et al., 2009; Muller et al., 2009; Stella et al., 2013), nitric oxide (NO; Rummel et al., 2002), nitrogen dioxide (NO2; Stella et al., 2013), nitrous oxide (N_2O; Eugster et al., 2007; Famulari et al., 2010; Jones et al., 2011) and aerosols (Nemitz et al., 2008; Ahlm et al., 2009; Farmer et al., 2011, 2013). This results in a low SNR and an increased overall uncertainty of the flux. Moreover, for measurements of all these gases, it is impossible co-locate sensor and anemometer. Closed-path sensors have inlet lines that can create a time lag (τ) between the vertical wind velocities (w) and measured scalar concentrations (c). The correction of the phase shifts between w and c by t data points (where $t = \tau$ ×sampling frequency) is a key step in the calculation of fluxes and it is routinely done by assessing the cross-covariance function between c and w, which reveals a maximum when the data are fully synchronized. However, when the random uncertainty is high, as is the case of all the gases, the cross-covariance becomes noisy, making the identification of a maximum very unclear. For VOCs fluxes, which often have low SNR, various options to determining time-lags have been proposed by Taipale et al. (2010). There are three approaches: the prescribed (PRES), maximum (MAX) and average (AVG) methods. The PRES method uses a constant time lag, which is predicted on the basis of the characteristics of the sampling system; the MAX method searches for the maximum value in the cross-covariance function between *w* and *c* within a predefined time window; the AVG method applies a centered running mean to the cross-covariance function and then selects the flux from the unsmoothed cross-covariance function that corresponds to the maximum of the absolute running mean. Because of different options available, the calculated fluxes may differ in function of the chosen time-lag method. In fact, Taipale et al. (2010) highlights that the use of a prescribed time-lag may underestimate the flux, as the "true" time-lag can vary over time due to fluctuations in pumping speed of the air to be sampled but also due to the degree of absorption/desorption onto the inlet walls that affects the effective transport time throughout the sampling tube. On the contrary, maximization of covariance within a noisy cross-covariance with multiple local maxima may well bias fluxes towards more extreme values (Laurila et al., 2012). The AVG method offers a sort of compromise between the two approaches, but some systematic bias still remains. However, the bias induced by maximization of the covariance is closely linked to the random error in the flux, which is in part due to the SNR of the instrumentation and may be greater than the systematic error induced by a prescribed time lag. Then, a method to quantify the random error in the flux, separate it into sampling and instrument error components, is needed. A measure of the random error that affect the flux, can be provided by the standard deviation of the covariance function $f_{w'c'}(t)$ for time lags far away from the true time lag *(t)* (Wienhold et al., 1995; Spirig et al., 2005, Equation 6):

$$RE_{\sigma} = \sigma_{fw'c'} [-I, +I]$$

Equation 6. Equation for flux random error as standard deviation of cross-covariance function for time lags far away from the true time lag.

where *I* is a region of the cross-covariance function far away from the point of zero time lag. Usually, *I* defines two regions of the cross-covariance function, one covering the positive time shifts and the other covering the negative time shifts ($-I = -150$ to -180 s and $+I = 150$ to 180 s). In order to estimate the flux measurement precision at a given confidence interval, the estimation of the random error must be multiplied by α ($\alpha = 1.96$ for the 95th percentile; $\alpha = 3$ for the 99th percentile) which can be used as the limit of detection (LOD) for the flux. This is because the flux LOD_σ does not only depend on the SNR of the measurements, but also varies with wind speed and atmospheric stability. Therefore, it is necessary to recalculate the LOD_σ for each (half-hour) averaging period considered to calculate an EC flux. Although by using this technique is possible to separate a "realistic" flux signature from the general noise of the covariance, the determination of the standard deviation is often done using arbitrary boundaries (e.g. −150 to 180 s and +150 to 180 s) or defined as some multiple of the integral timescale (Spirig et al., 2005). This approach to calculate the random uncertainty of a flux, is based on the concept that any correlation between c' and w' within these intervals of time-lag reflects the random noise in the time series or is due to organized structures that persist over much longer time, suggesting that turbulence is not stationary or statistically not well covered in the measurement. Furthermore, this method highlights if the scalar has a cross-covariance which remains positive or negative over wide ranges rather than fluctuate around zero. A variant of the LOD_σ approach is to calculate the random error based on the root mean squared deviation (RMSE) of $f_{w'c'}(t)$ from zero within the same specified region. Into flux computation, the random flux error can equal or even exceed the magnitude of the flux, introducing a bias as discussed above. In addition, when the algorithm continue to search a maximum in the cross-covariance, the derived flux may switch between emission and deposition values of similar magnitude. This phenomenon is called "mirroring" (Langford et al., 2015) and is showed in Figure 3 with example fluxes obtained using TDL, UH-SAS and PTR-MS. Then, the use of the MAX or AVG method enhance the mirroring effect, because these methods systematically choose the furthest point away from zero which in the extreme case can result in the very unnatural flux distribution. Instead, the use of PRES time lag eliminates the splitting of data among the two side of zero line giving a much more natural flux distribution. The last issue that remain unresolved, when mirroring effect is observed, it is if there are fluxes or sufficient statistics to resolve them.

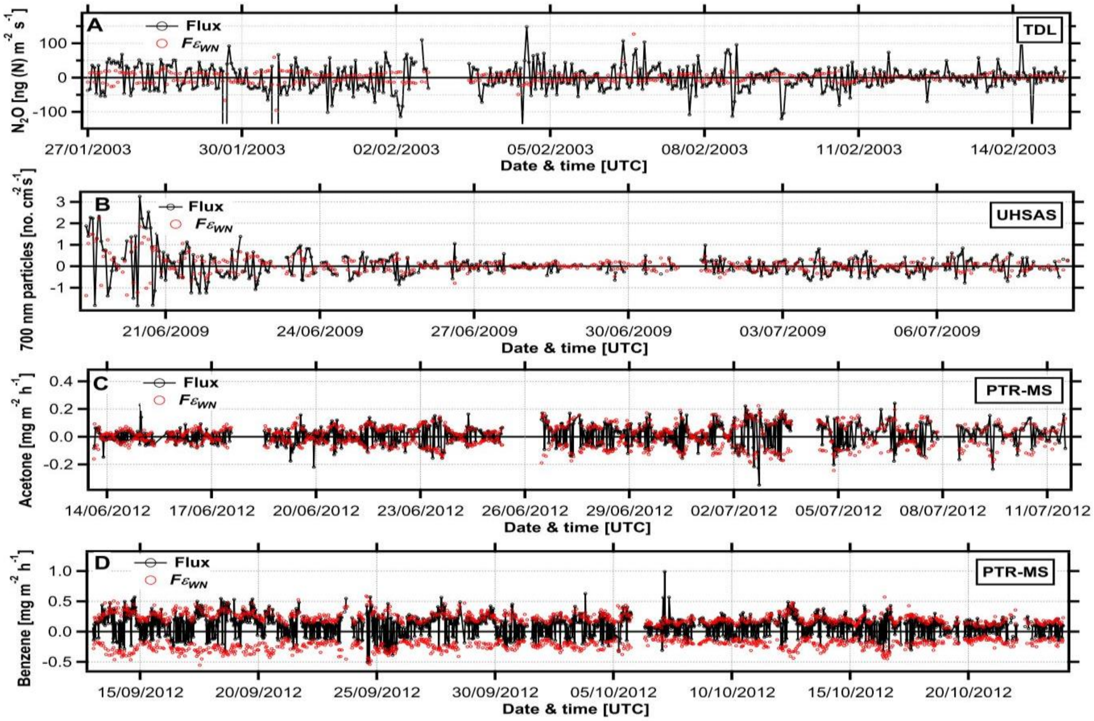

Figure 3. Example of "mirroring" in Eddy Covariance fluxes with low SNR processed with the MAX time-lag method. The data were obtained by TDL (A), UHSAS (B) and PTR-MS (C and D) instruments during four separate measurement campaigns (Langford et al., 2015).

If data in which mirroring occurs have to be utilized at a 30 min time resolution, they should be rejected because do not have enough significant information that exceed random uncertainty. However, averaging half-hour fluxes over longer observation period may provide the additional statistical information required for resolving fluxes. The statistical significance of averaged fluxes can be evaluated against the mean LOD_σ calculated from the LOD_σ values of the individual half-hour fluxes used for the average. For this reason, individual half-hour fluxes that fail specific LOD_σ criteria should not be discharged, as they may retain useful information on the net exchange when averaged and reported with random uncertainty estimation. Then, fluxes that fall within the LOD_σ interval cannot be resolved by the measurement system, but those fluxes that exceed this interval are significantly different from zero.

2.3. Ancillary measurements

In order to achieve a better understanding of the processes and relationships occurring in the agricultural ecosystem investigated in the second study case, other environmental variables are recorded along with VOCs fluxes. CO_2 and H_2O fluxes are measured using EC technique by coupling the same sonic anemometer used for VOCs fluxes with a closed-path infrared gas analyzer (IRGA). Moreover, meteorological data have been recorded: photosynthetic photon flux density (PPFD), air temperature (T) and relative humidity (RH), precipitation, irrigation and air pressure. Since the attention of the study focused on the VOCs exchange, biometrical determinations and phenology have been estimated through measurements of leaf area index (LAI) and aboveground biomass. While LAI has been estimated by detaching leaves and measuring their surface using an area meter, the aboveground biomass has been assessed by destructive sampling 1 m^2 of vegetation with six replicates in four plots randomly chosen among 15-18 m from the EC tower. LAI is estimated by detaching leaves and measuring their surface using an area meter. Biomass is determined gravimetrically by separately oven drying to constant weight the different plant parts (Vitale et al., 2009). Phenology was followed employing a phenological camera in the field and with weekly inspections in the field, referring to a phenological key.

2.4. Experimental sites

2.4.1. Landfill site

The landfill site is located in Giugliano municipality, in Campania region. The site is inside the area known to the chronicles as “Terra dei Fuochi”. This is an area of particular interest because of the twenty-year history of illegal waste dumping. More details about the site will be presented in the third chapter of this PhD thesis, where VOCs anthropogenic emissions by landfills will be discussed.

2.4.2. Agricultural site

The agricultural site is located in Borgo Cioffi, Eboli, province of Salerno in Campania region. This is the southernmost candidate to ICOS (Integrated Carbon Observation System) network and an interesting experimental and observation site for agricultural gases exchanges in the Mediterranean area. More details about the site will be presented in the fourth chapter of this PhD thesis, where BVOCs exchanges by an agricultural ecosystem, during a whole crop growing season, will be discussed.

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3. Results & Discussion

3.1. (1st study case). “Dynamics of anthropogenic VOCs emitted from illegally managed waste landfills”:


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Composition and emission of VOC from biogas produced by illegally managed waste landfills in Giugliano (Campania, Italy) and potential impact on the local population

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3.1.1. Punctual measurements: Composition and emission of VOC from biogas produced by illegally managed waste landfills in Giugliano (Campania, Italy) and potential impact on the local population.

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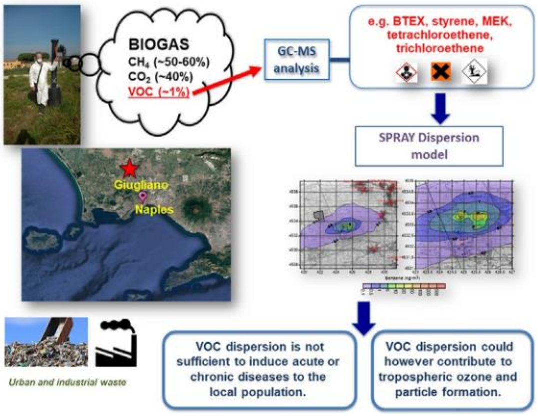
Abstract

The composition in Volatile Organic Compounds (VOC) of the biogas produced by seven landfills of Giugliano (Naples, Campania, Italy) was determined and VOC emission rates assessed to verify if these compounds repre- sent a potential threat to the population living nearby. VOC composition in the biogas could not be predicted, as heterogeneous waste was dumped from the late 1980s to the early 2000s and then underwent biological degradation. No data are available on the amount and composition of VOC in the biogas before the landfills closure as no operational biogas collection system was present. In this study, VOC composition was determined by gas chromatography–mass spectrometry (GC–MS), after collecting samples from collection pipes and from soil fractures in cover soil or capping. Individual VOC were quantified and data compared with those collected at two landfills in Latium, when they were still in operation. Relevant differences were observed, mainly due to waste aging, but no specific VOC revealing toxic waste dumping was found, although the concurrent presence of certain compounds suggested that dumping of industrial wastes might have occurred. The average VOC emission was assessed, and a dispersion model was run to find out if the emitted plume could affect the health of population. The results suggested that fugitive emissions did not represent a serious danger, since the concentrations simulated at the neighboring cities were below the threshold limits for acute and chronic diseases. However, VOC plume could cause annoyance at night when the steady state conditions of the atmosphere enhance pollutants accumulation in the lower layers. In addition, some of the emitted VOC, such as alkylbenzenes and monoterpenes, can contribute to tropospheric ozone formation.



Introduction

Biogas, the mixture of gases and vapors generated by biological de- composition of urban waste in landfills, is composed by ~50–60% of methane (CH4), ~40% of carbon dioxide (CO2) and ~1% of VOC (US EPA - Environmental Protection Agency, 2003; Zou et al., 2003). If directly released into the atmosphere biogas can have a significant impact on air quality (Al-Muzaini, 2009; Bogner and Matthews, 2003; Butt et al., 2008; Mor et al., 2006). For this reason, the EU issued a directive (1999/31/CE) aimed at defining the procedures to control biogas accumulation and migration in urban waste landfills, and the way biogas must be handled to minimize the impact on human health and environment. According to this directive, biogas emitted from collection pipes must be conveyed to a purification unit where a chiller and a filter re- move the condensable components, and then the biogas can be safely used for electricity generation. Monitoring of the pipelines and of possible fractures in the sealing system of compacted waste is also necessary to ensure that no fugitive emission occurs, because some of the minor biogas components, mainly VOC, are potentially toxic to human health (ATSDR - Agency for Toxic Substance and Disease Registry, 1997, 2000; Durmusoglu et al., 2010). Benzene and other aromatic com- pounds, together with alkenes, alcohols, furans, chlorinated com- pounds, carbonyls and cyclic alkenes (mainly monoterpenes), are in fact formed from biological waste decomposition (Allen et al., 1997). Carbonyls, cyclic alkenes and sulfur containing VOC are the main responsible of the biogas unpleasant smell (Keller, 1988; Kim et al., 2006; Komilis et al., 2004; Zou et al., 2003). The prolonged exposure to high VOC levels in the biogas produced by urban waste landfills can cause annoyance but can also damage people living nearby (Durmusoglu et al., 2010; Martì et al., 2014; Vrijheid, 2000). In particular, biogas emission can increase the levels of carcinogenic ben- zene up to exceed the air quality limits (5 μg m−3 for the annual average concentration) established for human health protection (EEA – European Environment Agency, 2008). Besides benzene, other aromatics (e.g. toluene, xylenes and styrene) are present in the biogas and can affect human health, even if their toxicity is lower than that of benzene (ATSDR - Agency for Toxic Substance and Disease Registry, 2000; IPCS –

International Programme on Chemical Safety, 1997). Chlorinated VOC such as trichloroethene and tetrachloroethene (PCE) are also of interest because of their potential carcinogenicity (ATSDR - Agency for Toxic Substances and Disease Registry, 1997; Haddad et al., 1999; Rusyn et al., 2014). Biogas emission is of particular concern in Campania, as hazardous waste of various types coming from all over Italy was illegally dumped in many of the landfills since the 80s (D'Alisa et al., 2010). The illegal dumping of toxic waste was so widespread in Campania that about 2500 contaminated sites have been identified so far, most of them lo- cated close to the urban area of Naples, which is characterized by the highest population density of the Southern Europe (Balestri, 2010). Severe episodes of soil and water contamination were reported in the landfills of Giugliano municipality, where fires also occurred causing a vast release of contaminants in the atmosphere (Balestri, 2010). Giugliano, with ca. 123,800 residents, is one of the most densely popu- lated city of Italy (1308 inhabitants for km2), thus, the presence of illegal of police investigations assessed that in Giugliano landfills intensive dumping of toxic waste was carried out over a long time causing a wide release of contaminants in the atmosphere, especially when arson occurred (Triassi et al., 2015). The sites were hence closed a de- cade ago by a court injunction, followed by a trial to identify and punish the responsible. While the long-term harmful effects of toxic contaminants released on water and soil are presently a matter of investigation (Mazza et al., 2015; Triassi et al., 2015), nothing is known about the composition of the biogas released in the atmosphere and its possible impact on human health. Local authorities expressed concern on this aspect, due to an increased amount of fugitive emission caused by the im- pairment of biogas management and leakages in the sealing system. To assess the potential risk represented by VOC emissions, the com- position of the biogas produced by each landfill in Giugliano municipality was determined and these emissions were compared with those emitted by two landfills, Malagrotta and Colleferro in Latium region, active at the time of sampling, where no evidence of illegal dumping of toxic wastes exists. Subsequently, a detailed reconstruction of the local meteorological conditions was obtained by high resolution simulations with the WRF meteorological model (Skamarock et al., 2008; http:// wrf-model.org), covering a year-long period which included the experimental campaigns. Hourly emission rates and meteorological data were finally fed into the Lagrangian three-dimensional particle dispersion model (LPDM) SPRAY (Anfossi et al., 2010; Tinarelli et al., 2013) to estimate short and long term potential health risks due to the possible exposure to typical pollutant concentrations. In the following work, data of the VOC composition in the effluents of seven Giugliano landfills are presented, together with the biogas possible impact on the health of people living nearby.

Material & Methods

Site description

The Giugliano municipality (40°55′54.77″N 14°11′44.05″E) is located in the northwest area of Naples, Italy, on a flat land. The climate is hot-summer Mediterranean according to the Köppen-Geiger classification (Peel et al., 2007), with a mean temperature of 23.4 °C during summer and 8.2 °C during winter, and a mean annual precipitation of 900 mm. Measurement campaigns were carried out at seven landfills located in the same municipality. These landfills were: Masseria del Pozzo, Ampliamento Masseria, Ampliamento Schiavi, Novambiente, Resit x, Resit 1b and Resit 2b (Table 1 and Fig 1). Masseria del Pozzo, Ampliamento Masseria, Ampliamento Schiavi and Novambiente are close to each other and occupy a total area of 32 ha. All sites have geocomposite capping and collection pipes, but no CH_4 recovery activity is currently operating, so the biogas spreads into the atmosphere. In a first terrestrial campaign, measurements were conducted every month from June 2015 to November 2016, collecting air samples from the biogas pipes and from fractures in the capping. We compared the average number and relative content of VOC with those present in the biogas emitted by the landfills of Colleferro and Malagrotta, located in the Latium region and active at the time of sampling, where no illegal practices were performed, and urban waste of similar composition was dumped. Colleferro, the only landfill still in operation today, became effective in biogas production in the late 1990s, and was sampled for 6 months in 2011–2012, when the maximum production of biogas and VOCs concentration were reached. Biogas was collected in various parts of the landfill, but for our purposes, the VOCs content in the biogas entering the filtration unit was the one that more closely approached the average fugitive emission of Giugliano. Malagrotta, the largest landfill in Europe until its closure in 2013, started to be active in the same years as the Giugliano ones, and it progressively expanded into several pits with different waste aging. We had the opportunity to sample the biogas in this landfill in the late 1990s, from two aged pits where biogas production was already declining. Waste age in these pits was comparable to that of the Giugliano landfills when they were still in operation. Similarly to Colleferro, the biogas was sampled in the main ducts at the inlet of the filtration unit. In both cases, urban waste treatment was the same as the one used in Giugliano landfills when they were in operation, and sampling and analysis procedures were as well the same.

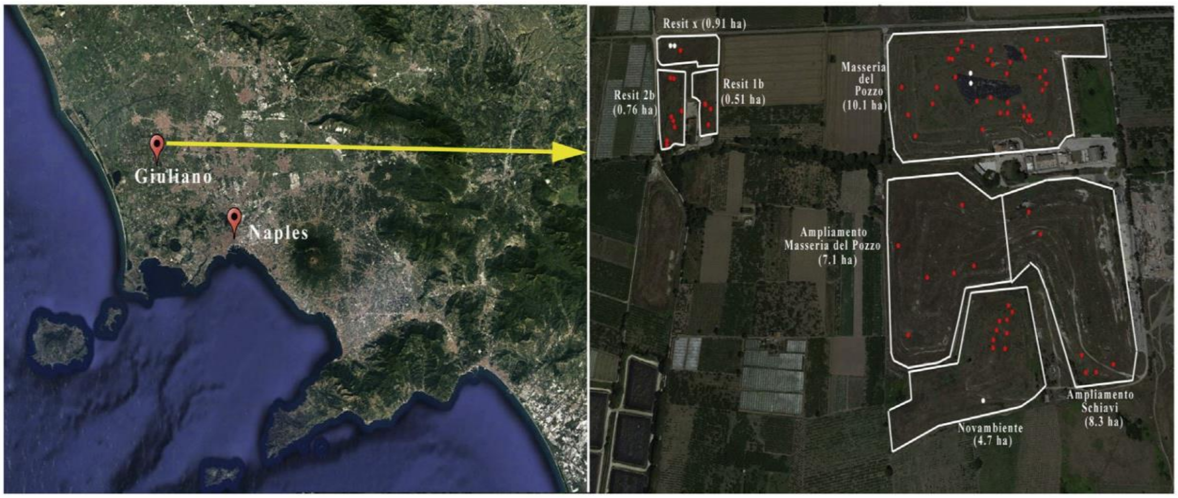
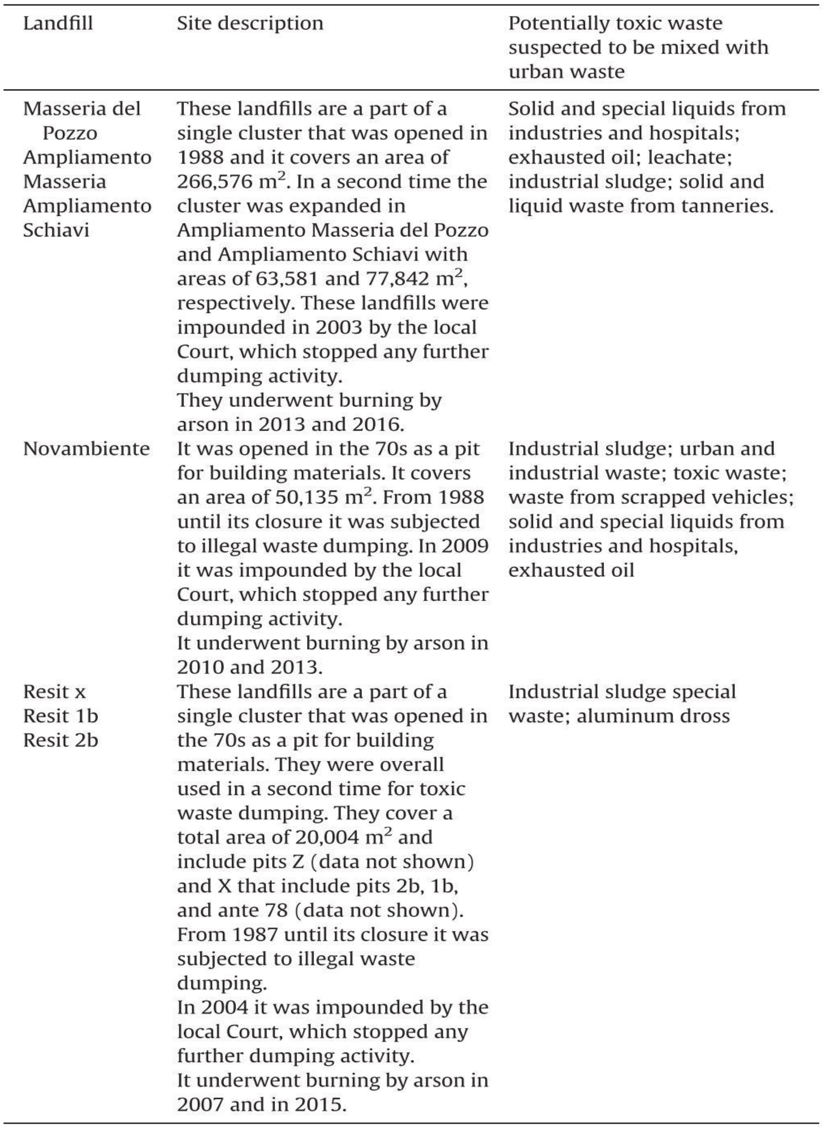


Fig 1. Map of the landfills of Giugliano Municipality, Campania, Italy. Red dots: sampling sites

VOC sampling and analysis

Biogas was sampled from the collection pipes of each landfill and from soil fractures (hot spots) causing fugitive emissions from major discontinuities in the capping material. The collection of air samples was carried out with adsorption tubes (8 cm × 0.3 cm i.d.) filled with Tenax GC© particles (200 mg; 35/60 mesh; Markes International, Ltd., Llantrisant, UK)



Landfill	Site description	Potentially toxic waste suspected to be mixed with urban waste
Masseria del Pozzo Ampliamento Masseria Ampliamento Schiavi	These landfills are a part of a single cluster that was opened in 1988 and it covers an area of 266,576 m^2. In a second time the cluster was expanded in Ampliamento Masseria del Pozzo and Ampliamento Schiavi with areas of 63,581 and 77,842 m^2, respectively. These landfills were impounded in 2003 by the local Court, which stopped any further dumping activity. They underwent burning by arson in 2013 and 2016.	Solid and special liquids from industries and hospitals; exhausted oil; leachate; industrial sludge; solid and liquid waste from tanneries.
Novambiente	It was opened in the 70s as a pit for building materials. It covers an area of 50,135 m^2. From 1988 until its closure it was subjected to illegal waste dumping. In 2009 it was impounded by the local Court, which stopped any further dumping activity. It underwent burning by arson in 2010 and 2013.	Industrial sludge; urban and industrial waste; toxic waste; waste from scrapped vehicles; solid and special liquids from industries and hospitals, exhausted oil
Resit x Resit 1b Resit 2b	These landfills are a part of a single cluster that was opened in the 70s as a pit for building materials. They were overall used in a second time for toxic waste dumping. They cover a total area of 20,004 m^2 and include pits Z (data not shown) and X that include pits 2b, 1b, and ante 78 (data not shown). From 1987 until its closure it was subjected to illegal waste dumping. In 2004 it was impounded by the local Court, which stopped any further dumping activity. It underwent burning by arson in 2007 and in 2015.	Industrial sludge special waste; aluminum dross

Table 1. Description of Giugliano landfills and type of illegal waste dumped. (From Balestri, 2010).

as reported in other landfill studies (Kim et al., 2006, 2008; Peng and Batterman, 2000; Sadowska-Rociek et al., 2009). Total air sampling volume was 100 ml air, which at our sampling conditions resulted as the optimal volume for achieving the greatest accuracy and avoiding breakthrough losses. A small pump (Pocket Pump SKC Inc., USA) was used to flow the air into the traps at a rate of 50 ml min−1. Prior to use, all prepared tubes were conditioned for 120 min at 280 °C with a flux of pure nitrogen gas. After sampling, all traps were stored at −20 °C to avoid chemical alteration of the retained VOC. Compounds were released by the traps using a Series 2 thermal- desorption unity (Markes International) at a helium flow rate of 50 ml min^{-1} at 250 °C for 15 min, then transferred from the Tenax trap into a cry focusing unit consisting of a short and smaller tube (13 cmin length) also filled with Tenax and kept at−30 °C. By a ballistic rapid heating of the cold trap from −30 to 280 °C compounds were transferred into a fused silica capillary column HP-1 (60 m × 0.25 mm I.D. × 0.25 μm film thickness) supplied by J&W Scientific (Agilent Technologies, Palo Alto, CA, USA) through an inert fused-silica capillary line heated at 200 °C. The GC separation was performed on a 7890A gas chromatograph coupled with a 5975C mass detector (GC–MS, Agilent Technologies, Wilmington, USA) for GC peak identification. VOC separation was performed by keeping the column at an initial temperature of 30 °C for 2 min and then by increasing the temperature at a rate of 6 °C min^{-1} up to a final temperature of 290 °C. The flow rate of carrier gas, high purity Helium (99.99%), was 1 ml min^{-1}. MS scans were performed by collecting positive ions from m/z 20 to 300, ionization voltage was 70 eV. Identification was achieved by combining the information of the relative retention times and fragmentation pattern of eluted compounds, using the sequence of elution reported in the data- base compiled by Ciccioli et al. (2002) of650 VOC identified in air. Iden- tified compounds were quantified by the external standard calibration approach using calibrated VOC gas cylinder containing known concentrations of different VOC (Apel-Riemer Environmental Inc., Broomfield, CO, USA), and liquid mixture of VOC solutions which were diluted at five concentration levels (Ciccioli et al., 2002; Martì et al., 2014). The precision of VOC analysis, quantified by triplicate analysis of the standard, varied among different species but was generally in a fewpercent- age range (4–8%). Blank emissions and artifact formation, which can affect method sensitivity and overall performance, were determined using clean tubes. The detection limit of VOC was commonly achieved at the 0.1 ng level. Relative response factors were determined for all the potentially toxic components, for a minority of them by interpola- tion techniques (Ahn et al., 2011). Overall, 67 collection pipes and 7 hot spots were investigated; in the former case the flow rate of gas re- leased was assessed by means a Velocicalc 8355 Air Velocity Meter (Tsi Incorporated, Shoreview, MN, USA), in order to compute mass emission fluxes.

Modelling of the VOC plume and procedure to assess hourly emission rate from landfills

During the biogas sampling, measurements of CH_4 fluxes were also conducted using the Eddy Covariance system. This system was installed on a 25m tall tower located at the southern edge of Masseria del Pozzo, at north edge of Ampliamento Masseria del Pozzo and Ampliamento Schiavi landfills. The analysis of long-term variability of CH_4 emissions showed a weak seasonal variability, while a significant daily cyclicality was detected, with daily maximum flux six times larger than nightly minimum values (data not shown). The observed variability was used to reconstruct daily time modulation of emissions. The allocation of total CH_4 emissions, measured by the eddy covariance tower, to the different landfills surrounding the measuring tower was based on the results of airborne campaigns realized with Sky Arrow ERA research aircraft (Gioli et al., 2004), equipped with a payload specifically assembled to monitor CH_4 fluxes when flying over the landfills area. Flights were repeated with monthly periodicity and post-processing of observed scalar concentrations and wind vector allowed to compute the atmospheric mass budget of CH_4 emitted by the area underlying flight trajectories (Alfieri et al., 2010; Gioli et al., 2014). A linear model was then applied to estimate the contribution of the different landfill groups to the total emission (Gasbarra et al., 2017). The CH_4 emission rates per unit area computed for the different landfills ranged from 0.3 to 0.4 g m^{-2} h^{-1}. Landfills age and type of waste dumped are the likely reasons for recovering CH_4 emissions lower than those recently measured over other European waste disposal sites, whose values fall in the range 1–5g m^{-2} h^{-1} (Di Bella et al., 2011; Riddick et al., 2018; Soporan et al., 2015). However, in a closedown landfill of Taiwan, the measured CH_4 emission value was 0.06 g m^{-2} h^{-1} (Hedge et al., 2003) while in Japan was 0.57 g m^{-2} h^{-1} (Ishigaky et al., 2005). To support the atmospheric dispersion modeling of emitted pollutants, hourly average emission values were calculated for each considered dumpsite during the period of interest. The hourly average emission rate of all the VOC species was estimated on the basis of CH_4 flux, considering their average concentration ratio within the biogas sampled over each of the studied landfills. The impact on air quality and possible related hazards for human health due to VOC emission were evaluated through the application of the LPDM SPRAY. Being not stationary, SPRAY adequately manages the local scale dispersion in a near costal area such as the one considered in this study, characterized by relevant space and time variability of dispersion conditions (Gariazzo et al., 2007; Giua et al., 2014). Moreover, the LPDM SPRAY is capable to describe atmospheric dispersion in low-wind conditions (Brusasca et al., 1992) that can cause high concentration of pollutants nearby ground level non-buoyant sources. In addition, LPDMs can precisely describe the irregular geometric structure of the emissions allowing a better simulation of the dispersed pollutants coming from the landfills. In this respect, a relatively high resolution was required to describe concentration distribution near the landfills, where maximum values are expected for non-buoyant surface level emissions. For the dispersion simulation, a computational domain of 12 × 12 km^2 with an horizontal grid spacing of 100 m was defined to include the nearest inhabited areas. Local meteorology was reconstructed by means of the WRF meteorological model (Skamarock et al., 2008; http://www.wrf-model.org/). Four nested grids were employed to reach the required high resolution over the target area, with horizontal grid spacing of 45, 9, 3 and 1 km respectively and 35 vertical levels up to 50 hPa. WRF results were com- pared with surface observations of the meteorological stations of Napoli-Capodichino and Grazzanise airports and of the sonic anemometer located on the eddy covariance tower at the southern edge of Masseria del Pozzo, showing a satisfactory reproduction of local meteorology space and time variability. A further downscaling up to the target resolution of 100m was achieved by employing the mass-consistent diagnostic model Swift (Finardi et al., 1993).

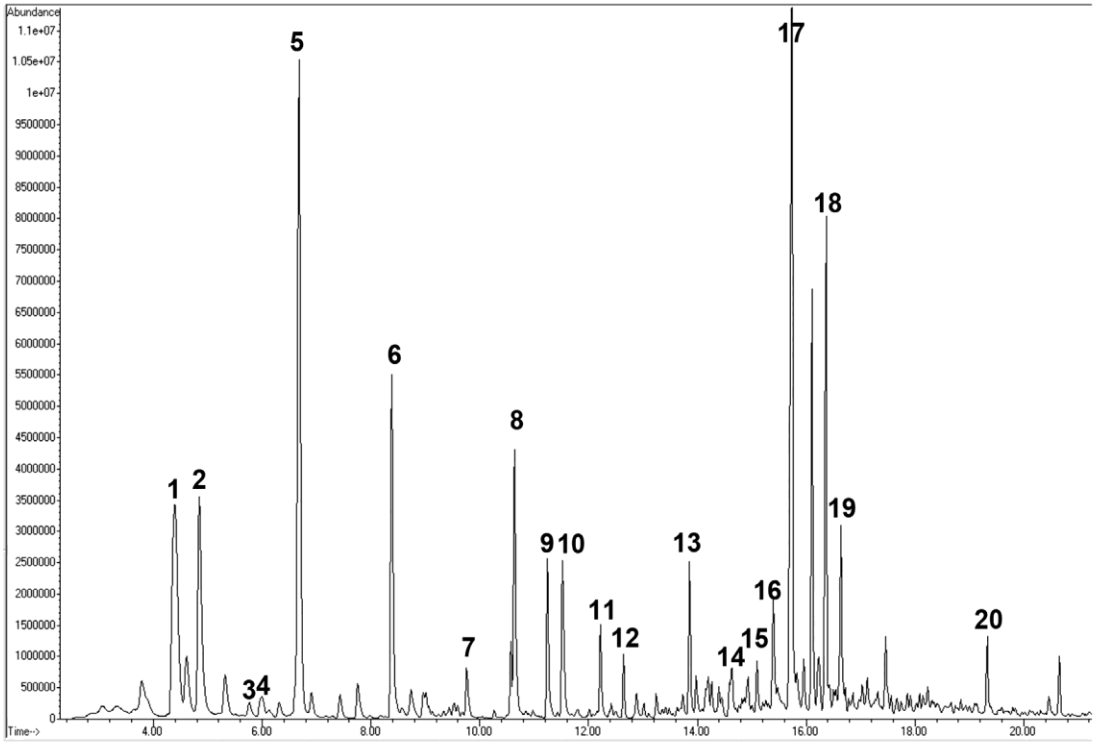
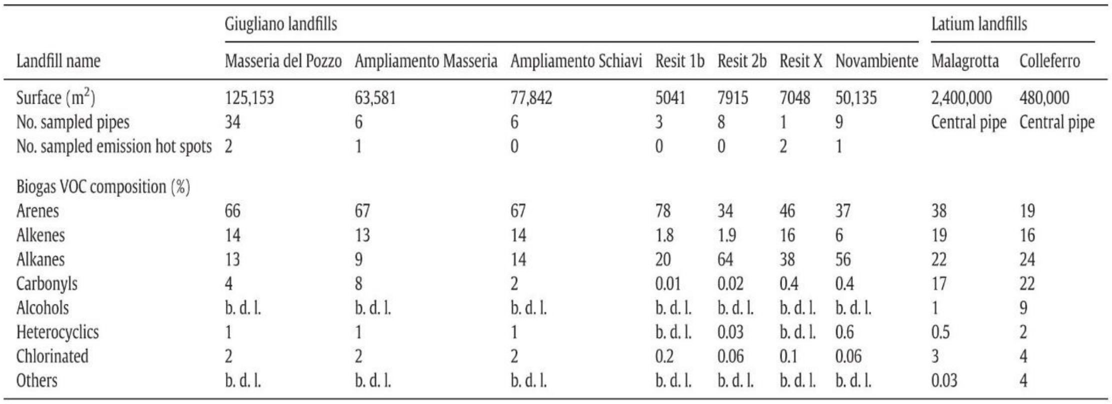


Fig 2. Typical GC–MS profile of the biogas emitted by Giugliano landfills. 1. 3-methyl pentane; 2. hexane; 3. methyl-cyclopentane; 4. benzene; 5. hexamethyl-disiloxane (bleeding); 6. toluene; 7. 2,4-dimethyl eptane; 8. hexamethyl-cyclotrisiloxane (bleeding); 9. ethylbenzene; 10. p +m-xylene; 11. styrene; 12. o-xylene; 13. octamethyl-trisiloxane (bleeding); 14. α-pinene; 15. o-ethyltoluene; 16. β-pinene; 17. 1,2,3-trimethyl benzene; 18. 1,2-dichlorobenzene; 19. Octamethyl-cyclotetrasiloxane (bleeding); 20. p-cymene; 21. limonene.

Result and discussion

VOC composition in the biogas

The biogas composition strongly depends upon the type of waste and the time it underwent biological degradation (Allen et al., 1997). About 160 compounds belonging to different chemical VOC classes were identified and quantified in the biogas of the various sites. This list does not include methyl silanols (Fig. 2) because, even if always present in the GC–MS profiles, their peaks are mainly due to the partial decomposition of the solid phase of the polysiloxanes coated capillary columns (column bleeding) and are thus difficult to quantify. Before looking in detail into the individual VOC emitted, differences in the main VOC classes were analyzed, to obtain some general indications on how biogas composition evolved after waste dumping ceased. The detected VOC were grouped in the following chemical classes: arenes, alkenes, alkanes, carbonyls, alcohols, heterocyclic compounds, chlorinated compounds and other compounds. Arenes group included all the aromatic compounds from benzene up to tetralkyl benzenes and benzene containing unsaturated groups. For practical reasons, naphthalene was also included in this group, although it is a polyaromatic hydrocarbon. Alkane group included linear, branched and cyclic components. The same approach was used to define the alkene class, including monoterpenes such as D-limonene and α-pinene, usually quite abundant in the biogas of urban waste landfills (Müller et al., 2004; Statheropoulos et al., 2005) due to the presence of vegetables and residues of household cleaning products (Allen et al., 1997; Schwarzbauer et al., 2002; Slack et al., 2005). In addition to linear aldehydes and ketones, other cyclic carbonyl compounds commonly associated with monoterpenes in plant emission and household cleaning products, such as menthone and camphor, were included in alkene class. Furans and thiophene were classified, instead, as heterocyclic compounds. Chlorinated compounds class included not only all saturated and unsaturated chlorine-containing volatiles, but aromatic compounds such as chlorobenzenes as well. The remaining compounds, characterized by different structures and functional groups, were grouped together as “other compounds”. In our case this class included some sulfur compounds, eucalyptol, an ether of natural origin, and trimethyl arsine, detected in some urban landfills (Pinel-Raffaitin et al., 2007).



	Giugliano landfills							Latium landfills	
Landfill name	Masseria del Pozzo	Ampliamento Masseria	Ampliamento Schiavi	Resit 1b	Resit 2b	Resit X	Novambiente	Malagrotta	Colleferro
Surface (m^2)	125,153	63,581	77,842	5041	7915	7048	50,135	2,400,000	480,000
No. sampled pipes	34	6	6	3	8	1	9	Central pipe	Central pipe
No. sampled emission hot spots	2	1	0	0	0	2	1		
Biogas VOC composition (%)									
Arenes	66	67	67	78	34	46	37	38	19
Alkenes	14	13	14	1.8	1.9	16	6	19	16
Alkanes	13	9	14	20	64	38	56	22	24
Carbonyls	4	8	2	0.01	0.02	0.4	0.4	17	22
Alcohols	b. d. l.	b. d. l.	b. d. l.	b. d. l.	b. d. l.	b. d. l.	b. d. l.	1	9
Heterocyclics	1	1	1	b. d. l.	0.03	b. d. l.	0.6	0.5	2
Chlorinated	2	2	2	0.2	0.06	0.1	0.06	3	4
Others	b. d. l.	b. d. l.	b. d. l.	b. d. l.	b. d. l.	b. d. l.	b. d. l.	0.03	4

Table 2. Mean percent composition of VOC organic classes (%) in the biogas of the Giugliano landfills, now all closed down, compared with two Latium landfills that were still in operation. b. d. l. = below detection limit.

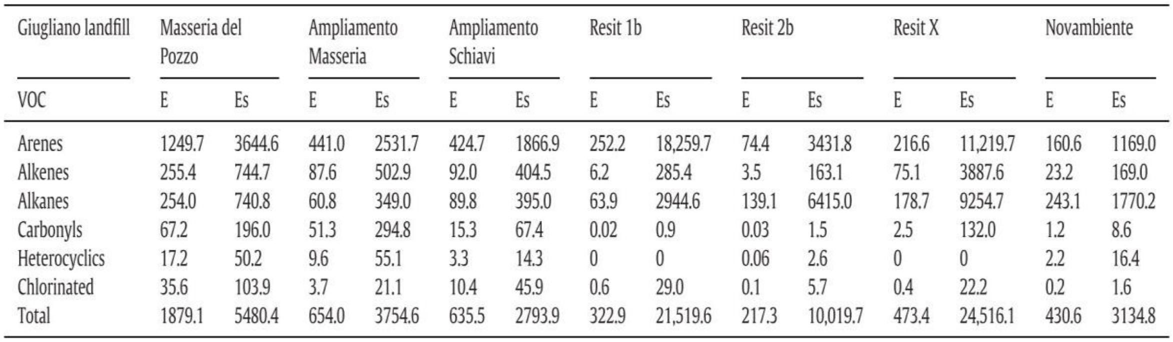
Table 2 summarizes the mean VOC biogas composition based on the most abundant chemical classes present, together with the type and number of sampling sites. The Giugliano landfills were grouped according to the managing companies. In these landfills, the relative composition of VOC classes showed a seasonal variability with a generally higher concentration in summer compared to winter. This variability was found mainly in the chemical classes of arenes, alkenes and alkanes detected in the sampled biogas of Masseria del Pozzo, Ampliamento Masseria and Ampliamento Schiavi. VOC concentration variations from winter to summer are highly related with temperature and moisture content, causing a rapid biological degradation of organic matter and the production of relatively large volumes of biogas within landfills (Chiriac et al., 2007; Zou et al., 2003). The relative composition of VOC classes in the Giugliano landfills was different from that of Latium active landfills in many aspects, but some systematic disparities were found. The biogas composition of Masseria del Pozzo, Ampliamento Masseria and Ampliamento Schiavi, managed by the same company, and of Resit 1b, was characterized by a high relative content of arenes, about 2–3 times higher than the one recorded in the two Latium landfills. Increased relative levels of arenes were mainly reflected by a decrease in the relative content of the other VOC classes. In particular, the alcohols were always below detection limit in the biogas of Giugliano landfills. Some common features were also found in the biogas composition of Novambiente and Resit

2b. These two landfills were managed by different companies and the relative content of alkanes in the biogas was, by far, the dominant one, as it exceeded by a factor varying between 2 and 3 the one measured in the Latium landfills. For Novambiente and Resit 2b, the increase in alkanes was concurrent with a dramatic drop in the relative content of alkenes and carbonyl compounds. According to Wu and Wang (2015), a very high relative content of alkanes in the biogas can be an indicator of a very advanced stage of biochemical waste degradation. Among the Giugliano landfills, Resit X was the only one with intermediate features compared to the other groups. Considering that the large arenes component of the biogas emitted by some of the Giugliano landfills could have implied an elevated relative content of highly toxic components (e.g. benzene and styrene), the low relative content of other VOC classes did not ensure that toxic compounds were not the dominant components. The results of the analysis of the single VOC are listed in Table S1. As previously reported for other landfills, waste composition and age influences biogas composition (Allen et al., 1997). The average relative content of benzene in the Giugliano landfill biogas is comparable to the one of the Latium landfills, with the highest levels found in Resit 2b and Resit X. The relative contents of styrene were, instead, one order of magnitude lower than those retrieved in both of the Latium landfills. The higher arenes content in the biogas of Masseria del Pozzo, Ampliamento Masseria and Ampliamento Schiavi was due mostly to dimethyl- and ethyl- substituted benzenes (mainly xylenes) and p-cymene (4-ethyltoluene). In particular, p-cymene content was low in the biogas of the younger Colleferro landfill, but already quite high in the biogas produced by the more aged waste of the Malagrotta landfill. P-cymene thus originated from the microbial transformation of monoterpenes, such as limonene (Davoli et al., 2003); high p-cymene content can be taken as an indication of a prolonged anaerobic waste degradation in these Giugliano landfills. The secondary origin of p-cymene was consistent with the lower relative content of limonene in the biogas released by the Giugliano landfills compared to that of the biogas produced by both Latium landfills. Although in smaller amounts, p-cymene was also detected in the biogas of those Giugliano landfills where alkanes were by far the dominant components. Quite high relative p-cymene contents were measured in the biogas of the Novambiente landfill, whose alkene fraction was strongly depleted in D-limonene. The selective biochemical conversion of D-limonene into p-cymene was further supported by the different relative contents of α-pinene and D-limonene in the biogas produced by the Giugliano and Latium landfills. While α-pinene was generally the dominant alkene in the biogas of all Giugliano landfills, D-limonene was the dominant component in the biogas of Latium landfills, where alkenes other than monoterpenes were also present. These findings further support the statement of Termonia and Termonia (1999) according to which a high relative content of D-limonene in the biogas is highly indicative of a limited bio-chemical waste aging. The structure of p-cymene closely relates to that of monoterpenes, and this compound is also directly emitted to a small extent in urban waste landfills because it is present in some terrestrial plants, especially conifers (Hakola et al., 2012; Kesselmeier and Staudt, 1999). Although responsible of the unpleasant smell of aged waste (Orzi et al., 2010), this compound is not toxic in the vapor phase, but has a great potential of ozone production. Additional information on waste degradation stage was obtained by comparing the type and contents of some chlorinated components (e.g. 1,1-dichloroethene, 1,2-dichloroethene, trichloroethene, tetrachloroethene and 1,2-dichloro-benzene) present in the biogas of the Giugliano and Latium landfills. These components are common constituents of the biogas produced by urban waste, as they come from the disposal of solvents used as degreasers and cleaners in indoor and industrial activities (Dincer et al., 2006; Guha et al., 2012). The number of chlorinated components in the biogas decreased with waste aging: saturated components such as alkyl halides (e.g. dichloromethane, dichloroethane etc.) present in the biogas produced by the younger waste of Colleferro were already below the detection limits in the biogas produced by the more aged Malagrotta waste (Table S1). The decrease of chlorinated compounds with aging can thus explain why in Resit 2b, Resit 1b, Resit X and Novambiente they were represented only by very limited amounts of 1,2-dichlorobenzene. This compound is probably well preserved even in very aged waste because of its high thermal stability (Chin et al., 2009; Young and Voorhees, 1992) and low water solubility. Only in the biogas of Masseria del Pozzo, Ampliamento Masseria and Ampliamento Schiavi, the presence of di-, tri- and tetrachlorethenes was detected, with the lower homolog as the dominant component. Since the presence of 1,1-dichloroethene in the biogas of the Latium landfills, and in other legally managed landfills (Dincer et al., 2006; Eklund et al., 1998), was always a minor component and tri- and tetrachloroethenes, together with 1,2-dichloroethene, were the dominant ones, only two hypotheses can be formulated to explain the higher content of 1,1-dichloroethene in the biogas of these three Giugliano landfills. 1,1-Dichloroethene of industrial origin could have been illegally dumped in these landfills, together with other industrial solvents. This might also explain the high relative content of m- and p-xylenes in these landfills biogas. Mixtures of xylenes (xylols) are in fact common components of ink, rubber, and adhesives. In thinning paints and varnishes, xylenes can be used as substitutes for toluene when slower drying is desired, thus xylenes are used in solubility testing by art objects conservators. Conversely 1,1-dichloroethene could come from a degradation reaction of the higher homologs, or from conversion of the 1,2 isomers. Although the biochemical degradation of tetrachloroethene to form trichloroethene was documented by Little et al. (1988) and further degradation of trichloroethene is, in principle, possible, no data exists indicating that 1,1-dichloroethene is formed through this pathway. Therefore, the higher levels reached by 1,1-dichloroethene in the biogas of Masseria del Pozzo, Ampliamento Masseria and Ampliamento Schiavi, seemed to be related more to illegal dumping of solvents than to biological degradation of urban waste. 1,1-Dichloroethene is certainly one of the compounds that need to be considered in evaluating the impact on the population living in the proximity of the Giugliano landfills, due to its toxicity and potential carcinogenicity (ATSDR - Agency for Toxic Substances and Disease Registry, 1994). Analogous considerations can be made on the composition of carbonyls in the biogas of the Giugliano landfills. While the presence of camphor, and/or menthone is consistent with the disposal of vegetables and household cleaning products, and is also found in the biogas of the Latium landfills, the high relative content of 2-butanone (or MEK) in the biogas of the same Giugliano landfills characterized by high levels of 1,1- dichloroethene and xylenes had two possible explanations. MEK could have been dumped together with other industrial solvents in the landfills of Masseria del Pozzo, Ampliamento Masseria and Ampliamento Schiavi, managed by the same company. MEK, similarly to 1,1- dichloroethene and xylenes, is in fact a common solvent in industrial processes involving gums, resins, cellulose acetate, and cellulose nitrate production. MEK is also used in synthetic rubber industry, in the production of paraffin wax, and in household products such as lacquer and varnishes, paint remover and glues.

Conversely, MEK could derive from extensive biochemical waste degradation. However, the absence of MEK in the biogas of Novambiente, and of Resit X, strongly supported the hypothesis that MEK was one of the industrial solvents illegally dumped in the Masseria del Pozzo, Ampliamento Masseria and Ampliamento Schiavi landfills. The co-occurrence at trace levels of 4- methyl-2-pentanone (MIBK), another common industrial solvent, supported this hypothesis. Quite interesting were also the compositional features of the heterocyclic compounds in the biogas of the Giugliano landfills, because relative contents of 2-methylfuran and 2,5-dimethyl furan equal or higher than those detected in the biogas of the two Latium landfills were measured in the biogas of Masseria del Pozzo, Ampliamento Masseria and Ampliamento Schiavi. In these landfills, the relative contents of these two components were much higher than tetrahydrofuran, one of the dominant components in the heterocyclic fraction of the Latium landfills biogas. Although higher levels of 2- methylfuran were possibly due to the enhanced decomposition of fibers and sugars in urban aged waste, the lack of this component in the more aged waste of Resit 1b, Resit 2b and Novambiente, where alkanes were the dominant components, suggested that 2-methylfuran was as well illegally dumped in these landfills. 2-Methylfuran is, indeed, a solvent widely used in pharmaceutical industry for the manufacturing of many common drugs and for the synthesis of vitamin B1. It is also used in the manufacture of methyl furfural, aliphatic compounds and sulfur and nitrogen heterocycles, and for producing pesticides, flavors or fragrances. Considering the class “other compounds”, none of the components found in the biogas of Latium landfills was detected in the biogas of the Giugliano landfills. Particularly important was the lack of trimethylarsine, since it is a genotoxic and carcinogenic compound (Andrewes et al., 2003) found instead at trace levels in the biogas of the Malagrotta landfill.

Concentrations and emission rates of VOC from the Giugliano landfills

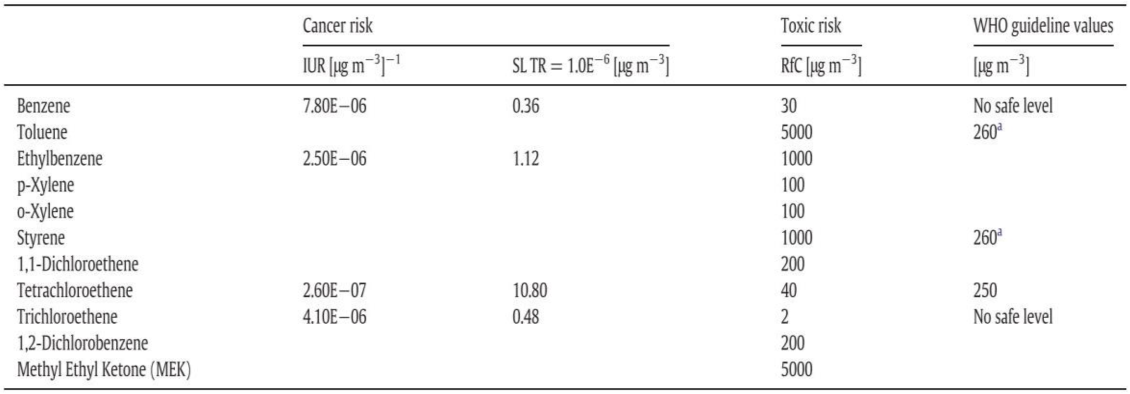
Although the potential impact on human health of VOC detected in the biogas of Colleferro and Malagrotta landfills could have been definitely higher than that of the Giugliano landfills for the presence of hazardous compounds, most of the toxic



Giugliano landfill	Masseria del Pozzo		Ampliamento Masseria		Ampliamento Schiavi		Resit 1b		Resit 2b		Resit X		Novambiente	
VOC	E	Es	E	Es	E	Es	E	Es	E	Es	E	Es	E	Es
Arenes	1249.7	3644.6	441.0	2531.7	424.7	1866.9	252.2	18,259.7	74.4	3431.8	216.6	11,219.7	160.6	1169.0
Alkenes	255.4	744.7	87.6	502.9	92.0	404.5	6.2	285.4	3.5	163.1	75.1	3887.6	23.2	169.0
Alkanes	254.0	740.8	60.8	349.0	89.8	395.0	63.9	2944.6	139.1	6415.0	178.7	9254.7	243.1	1770.2
Carbonyls	67.2	196.0	51.3	294.8	15.3	67.4	0.02	0.9	0.03	1.5	2.5	132.0	1.2	8.6
Heterocyclics	17.2	50.2	9.6	55.1	3.3	14.3	0	0	0.06	2.6	0	0	2.2	16.4
Chlorinated	35.6	103.9	3.7	21.1	10.4	45.9	0.6	29.0	0.1	5.7	0.4	22.2	0.2	1.6
Total	1879.1	5480.4	654.0	3754.6	635.5	2793.9	322.9	21,519.6	217.3	10,019.7	473.4	24,516.1	430.6	3134.8

Table 3. Total daily emission rates (E, g d^{-1}) and surface normalized total annual emission rates (Es, mg m^2 y^{-1}) of the VOC classes produced from the Giugliano landfills.

components present in the Latium landfills were removed by condensation and filtration, and the few remaining were partly converted into CO_2 and water in the internal combustion processes used for generating energy. In the Giugliano landfills, the condensation and filtration system for the gas was not in operation since the landfills were closed, so the biogas produced was directly emitted into the atmosphere either from the collection pipes, whose valves were in some cases open or leaking, or from hot spots of preferential fugitive emission, such as fractures in the overlaying capping cover, which was even absent in Resit caves. Gas migration between landfills could not either be excluded. In this situation, it was thus important to know the VOC concentration in the biogas in each of the Giugliano landfills and the amount ofmVOC released in the atmosphere. Table 3 compares the total daily emission rates of the various VOC classes in the biogas of the Giugliano landfills and the total annual emission rates produced per unit surface area. No clear correlation was found between the gas composition and the total annual emission rates normalized to the landfill surface. Particularly striking was the difference of one order of magnitude in the surface normalized VOC emission measured in Resit 2b and Novambiente, showing a similar VOC composition in the biogas. The fact that the surface normalized emission differed so much indicated that the biogas pressure inside the landfills was different. This might be due to several factors. The uncapped caves of Resit are expected to emit more than capped landfills. Among the capped landfills, at a limited fracturing corresponded a higher pressure in the collection pipes, and thus a stronger biogas flow, regardless of waste aging. Biogas diffusion between landfills could also explain a decrease in pressure and changes in biogas production. Whichever the explanation is, data showed that most of the VOC emission from the Giugliano landfills was determined by the smaller ones, whose surface normalized emissions were higher than the larger ones by one order of magnitude. To assess the potential impact on people living at the landfills borders, the VOC plume generated by these emissions was modeled. The compounds considered in the simulation are listed in Table 4. Although the National Legislation defining the Air Quality of the atmosphere poses specific limits only to the concentration of benzene in air, the potential impact of other components present in the landfill plume could not be ignored as some of them have adverse effects on human health or are carcinogens.



	Cancer risk		Toxic risk	WHO guideline values
	IUR [μg m^{-3}]$^{-1}$	SL TR = 1.0E^{-6} [μg m^{-3}]	RfC [μg m^{-3}]	[μg m^{-3}]
Benzene	7.80E−06	0.36	30	No safe level
Toluene			5000	260[a]
Ethylbenzene	2.50E−06	1.12	1000	
p-Xylene			100	
o-Xylene			100	
Styrene			1000	260[a]
1,1-Dichloroethene			200	
Tetrachloroethene	2.60E−07	10.80	40	250
Trichloroethene	4.10E−06	0.48	2	No safe level
1,2-Dichlorobenzene			200	
Methyl Ethyl Ketone (MEK)			5000	

Table 4. VOC used to assess the potential health impact of the emission plume generated by the Giugliano landfills. IUR: Inhalation Unit Risk; SL TR = Screening level Target Risk 10^{-6}; RfC: Reference Concentration; Values collected from: ISS/INAIL, 2014; US EPA - Environmental Protection Agency, 2017; WHO - World Health Organization, 2000. [a] (Weekly average).

Dispersion of the VOC plume and potential impact of human health

Specifically, in this work my contribution was mainly to measure VOCs composition, concentrations and emission rates used for the simulaton model. However, in the following section results of the modelling will be reported.

Model simulations covered a year-long period (from 01/11/2015 to 31/10/2016), including a large fraction of the experimental campaigns, allowing an estimation of the mean and maximum pollutants concentrations. In the simulations, the emission rates of the individual landfills were properly scaled, in order to fit with the continuous CH_4 flux determination obtained from eddy covariance measurements over the site. Due to the features of the chemical species emitted and to their limited atmospheric transport time over the considered area, pollutants were assumed to be non-chemically reactive. Although this strategy might have overestimated their impact, it allowed to apply local scale modeling capable to better describe the evolution of the VOC plume in non-homogeneous terrain conditions, to account for the VOC contribution from each individual landfill, and to get a satisfactory resolution nearby the landfill bodies and the nearest inhabited areas. Results showed that annual mean benzene concentrations inside the landfill area were lower than 30 ng m^{-3} (Fig. 3) with the highest values found over and around Resit landfills, where hourly averaged concentrations reached a maximum of 303 ng m^{-3}. Concentrations decreased significantly in the surrounding areas, where maximum hourly values of 10–20 ng m^{-3} were reached in the unpopulated area at the landfill border. The concentration values predicted by the model were much lower than the atmospheric limit of 5 μg m^{-3} fixed by the air quality standards. The estimated concentrations were also lower than the 360 ng m^{-3} exposure level, corresponding to the screening level risk of one occurrence over a million (Table 4). Model simulation estimated concentrations of o-xylene (not shown) slightly higher than those obtained for benzene, while toluene, p-xylene, ethylbenzene and MEK concentrations were about one order of magnitude higher than those of benzene. The space distribution of these VOC was quite similar, with some differences in the proximity of the landfills due to the landfills different emission rates. Annual mean concentrations reached values of 100 ng m^{-3} for toluene, ethylbenzene, MEK, and 200 ng m^{-3} for p-xylene (Fig. 4) nearby the landfills, where the maximum hourly average concentration exceeded 1 μg m^{-3} for toluene, ethylbenzene, MEK, and 2 μg m^{-3} for p-xylene. The nearest residential area (Parete) was influenced by yearly average concentrations of about 1 ng m^{-3} for toluene, ethylbenzene, MEK, and 2 ng m^{-3} for p-xylene. Maximum hourly concentrations reached over the same area were 200 ng m^{-3} for toluene, ethylbenzene, MEK, and 300 ng m^{-3} for p-xylene. All the computed concentrations were by far lower than the reference thresholds for toxic non-carcinogenic risk and WHO guideline values reported in Table 4. Estimated annual average concentrations of ethylbenzene were much lower than values causing a cancer risk of one case over a million in the exposed population. Only the maximum of the hourly average concentrations estimated during the whole simulated year reached values of the same order of cancer risk thresholds (~1 μg m^{-3}; Table 4) over the landfills bodies. Concentration values estimated by model simulation for the other toxic VOC listed in Table 4 (styrene, 1,1-dichloroethene, tetrachloroethene, trichloroethene, 1,2-dichlorobenzene) were orders of magnitudes lower than those of benzene and toluene. Styrene, 1,1-dichloroethene and tetrachloroethene showed annual average concentrations reaching about 1, 9 and 5 ng m^{-3} respectively over the landfills, where maximum hourly average concentrations were in the range 10–100 ng m^{-3}. Trichloroethene and 1,2-dichloro-benzene levels resulted lower than those of styrene by one order of magnitude. For all these compounds, concentrations were by some orders of magnitude lower than the threshold values of cancer and non-cancer risk (Table 4) although it cannot be excluded that emissions might be a source of annoyance when stable conditions are established over the site. A field campaign would be advisable to verify and confirm the atmospheric dispersion model results. Considering that toluene and its upper homologs, especially p-cymene, together with residual monoterpenes react much faster than benzene with OH radicals, the emission from the Giugliano landfills might contribute to increase the ozone air content once it gets mixed with the numerous sources of VOC and NOx active within the Naples-Caserta area. Besides vehicular emission, the most important sources of VOC in the area are: ship traffic in the port and gulf of Naples, biomass burning in small domestic heating appliances active in the countryside, open burning of illegal waste, and forest fires, which have plagued all the Vesuvius and other natural vegetation covered areas.

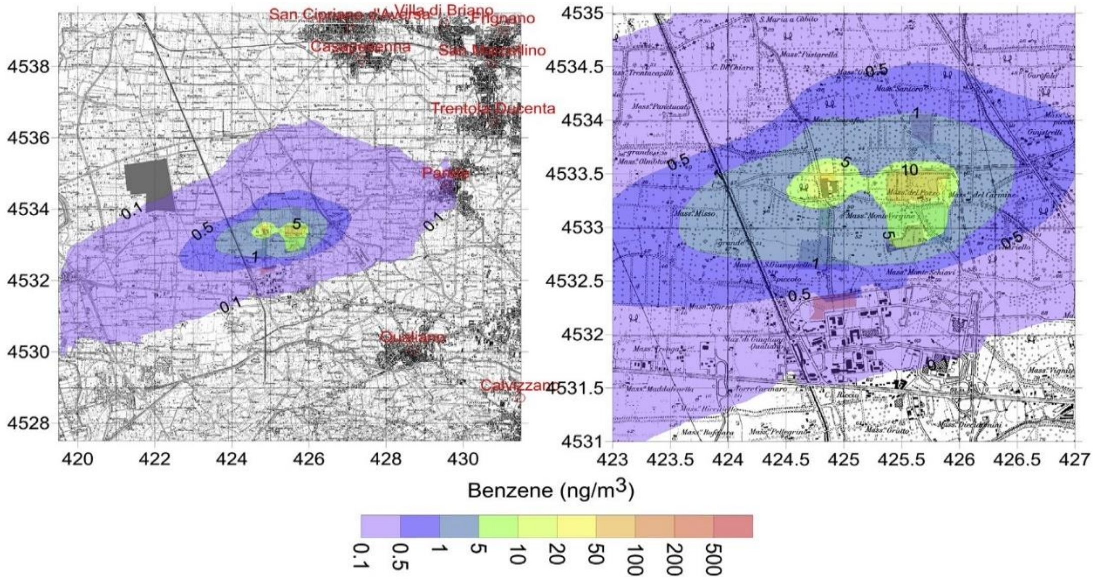


Figure 3. Benzene annual average concentration (ng/m^3) over the whole computational domain (left) and zoomed over a 4 × 4 km^2 area surrounding the landfills (right).

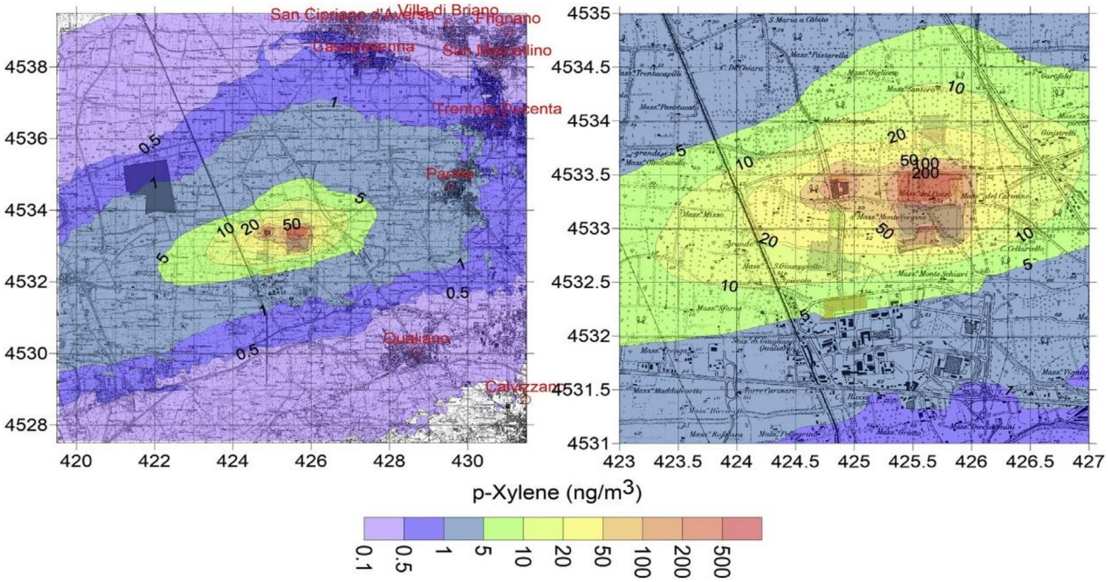


Figure 4. p-Xylene annual average concentration (ng/m^3) over the whole computational domain (left) and zoomed over a 4 × 4 km^2 area surrounding the landfills (right).

Conclusions

This study showed that toxic compounds were certainly present in the gaseous emission of the Giugliano landfills, and some of them seemed to be associated with past dumping of toxic waste. However, the potential impact of toxic substances on human health estimated by year-long atmospheric dispersion modeling showed that their emission rates were not sufficient "per se" to induce acute or chronic diseases in the local population. Landfill VOC emissions could however contribute to ozone and particle formation when mixed with all the other VOC, NOx and particle sources active within the Naples-Caserta territory. Although all of these landfills are no longer in operation, they must be kept under control to check that no increase in VOC fugitive emissions due to fracturing of the sealing system takes place, increasing the risks of fires and explosions. Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.05.318.

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3.1.2. Continuous real-time measurements: Qualitative VOCs burden and real-time concentrations kinetics in illegally managed waste landfills by Proton Transfer Reaction Time-of-Flight Mass Spectrometry. Manco et al. (in preparation)

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Abstract

Volatile organic compounds (VOCs) comprise only a small amount of the overall emitted landfill gases. However, they can diffuse into the atmosphere affecting tropospheric chemistry and regional air quality, representing a risk for human health. This study aims to investigate the qualitative VOCs burden into biogas and their concentrations variation during a continuous period on a landfill site in the area known as "Terra dei fuochi". In this particular region in Southern Italy, urban waste combined with industrial toxic material has been illegally dumped for decades. In order to obtain a real-time VOCs detection, we used a recently developed Proton Transfer Reaction Time-of-Flight mass spectrometer (PTR-TOF-MS). Results showed that the group of protonated ions related to VOC and/or fragment of VOC having an m/z between 31-69 group is the most representative in summer (95 %). Furthermore, oxygenated-VOC were the most abundant VOC to be detected, dominate by acetic acid (0.9-53 µg m^{-3}) and methanol (0.2-23.4 µg m^{-3}). Arenes are quite abundant in summer and during daytime, dominate by toluene (0.02-14.3 µg m^{-3}). Terpenes and sulfur compounds show higher concentration during autumn, suggesting they undergo photo-oxidation process in

summer. MEK (0.1-3.3 µg m^{-3}) show a similar trend in both seasons, related to solvent dumping along with arenes. Acetonitrile rarely reporting in landfill site, is always present in very low concentrations (0.01-1.7 µg m^{-3}). This study investigated, for the first time, the qualitative composition of VOCs burden into biogas and their real-time concentration fluctuations in illegally managed waste landfills employing PTR-TOF-MS.

Introduction

Landfill gases are naturally generated from waste decomposition and they are mainly represented by methane (∼50-60%), carbon dioxide (∼40%), and small quantities of other gases present in the landfill plume. These trace components (∼1–2%) are non-methane volatile organic compounds (VOCs) (Zou et al., 2003; Themelis and Ulloa, 2007). Quite recently, considerable attention has been paid to collection, analysis and characterization of airborne VOCs into landfill emissions, because these minor biogas components are potentially toxic to human health. Indeed, VOCs are among the major air pollutants due their malodorous (Davoli et al., 2003) and hazardous properties (Durmusoglu et al., 2010). Their nature and concentrations depend on the composition of deposited waste and on chemical and biological processes occurring in solid waste. Benzene and other aromatic compounds are in fact formed from biological waste decomposition (Knox, 1990; Allen et al., 1997), together with alkenes, alcohols, furans, chlorinated compounds, carbonyls and cyclic alkenes (mainly monoterpenes). Previous studies indicated that in urban atmosphere, the aromatic compounds, especially ethylbenzene and xylene, are related to the emissions from gasoline vehicles and gas stations (Cohen et al., 1991; Baldasano et al., 1998). Nevertheless, the landfill emission contribution to the current atmospheric VOC concentration is one of the most important sources besides industrial and vehicle sources (Zou et al., 2003). Biogas emission is an important issue in Campania area (Italy), as hazardous waste of various types was illegally dumped in many of the landfills since the early 1980s (D’Alisa et al., 2010). The illegal dumping of toxic waste was so widespread in Campania that about 2500 contaminated sites were identified so far; most of them located near the urban area of Naples called “Terra dei Fuochi”, characterized by the highest population density of the Southern Europe (Balestri, 2010). Several years of police investigations assessed that in Giugliano landfills intensive dumping of toxic waste was intensively carried on over a long time (Triassi et al., 2015). However, little is known about the chemical composition of the biogas released in the atmosphere by these landfills and its possible impact on the human health.

The key limitation of this research often is the lack of a sensitive and robust method for the real-time analysis of the VOCs released. One of the most promising techniques is certainly PTR-MS (Proton Transfer Reaction-Mass Spectrometry). PTR-MS has been already applied in many studies ranging from breath analysis to environmental monitoring and, recently to issues related to waste management and odorant emission control (Feilberg et al., 2010; Hansen et al., 2012), allowing the monitor VOCs concentrations in real-time. In particular, the recent introduction of time of flight (TOF) detector, coupled with Proton Transfer Reaction-Mass Spectrometry (PTR-TOF-MS, Jordan et al., 2009) indicates the possibility to maintain the high sensitivity and to provide, at the same time, improved time resolution (0.1 s), mass range (virtually unlimited) and mass resolution. This latter aspect allows the separation of isobaric compounds and the identification of the exact mass weight which allows to have the sum formula information.

The aim of this paper is threefold: a) to investigate the potentiality of PTR-TOF-MS as a tool for the real-time, direct and high sensitive monitoring of dynamic of VOC from a landfill site, (b) to investigate the qualitative VOCs burden into biogas emitted by the landfill site and (c) to investigate VOCs concentrations fluctuations during a continuous period.

Material and Methods

Site description

The landfill site is the same described in the section 3.1.1. in this chapter (Carriero, et al., 2018). In this study, all the measurements were carried out over four of the seven landfills described before, sampling air from the 25m taller tower at the southern edge of Masseria del Pozzo and at north edge of Ampliamento Masseria del Pozzo, Ampliamento Schiavi and Novambiente landfills. Continuous air sampling was conducted by PTR-TOF-MS, on elected weeks in July (20-27) and October (03-11) in 2016. Meteorological data (Table 1 and Table 2) were also recorded during the sampling period, to evaluate the influence of the seasonality on the VOCs emissions and to choose the typical day upon which carry out the qualitative analysis of VOCs burden. Meteorological data for October come from an ARPAC (regional agency for environmental protection) station in the area.

Date	Temperature [a] (C°)	Radiation [a] (w/m^2)
20/07/16	26.09 (0.99)	253.26 (71.61)
21/07/16	25.25 (0.92)	250.25 (70.42)
22/07/16	24.82 (1.00)	245.60 (67.87)
23/07/16	26.49 (0.99)	241.87 (66.68)
24/07/16	23.12 (0.35)	49.86 (17.01)
25/07/16	22.54 (0.64)	145.26 (43.35)
26/07/16	23.83 (0.95)	241.93 (66.66)
27/07/16	25.29 (0.72)	234.24 (66.88)
28/07/16	25.22 (0.61)	218.31 (60.94)

Table 1. Meteorological conditions during sampling days into the selected week of July 2016.

[a] Mean + standard error in parenthesis

Date	Temperature [a] (C°)	Radiation [a] (w/m^2)
03/10/16	21.00	147.34
04/10/16	20.20	171.65
05/10/16	18.30	187.43
06/10/16	16.60	127.29
07/10/16	17.20	140.42
08/10/16	17.50	174.62
09/10/16	18.60	129.02
10/10/16	18.50	144.96
11/10/16	14.70	57.07

Table 2. Meteorological conditions during sampling days into the selected week of October 2016.

[a] Mean

PTR-TOF-MS instrumental set-up

Proton Transfer Reaction "Time-of-Flight" Mass Spectrometer (PTR-TOF-MS) (Ionicon, Innsbruck, Austria) is composed of an ion source coupled with a drift tube and a high mass resolution time-of-flight mass spectrometer TOF-MS (Jordan et al., 2009; Graus et al., 2010). VOCs are detected in real-time through proton transfer reactions occurring between the H_3O^+ ions produced within the ion source and the sample gas inserted into the drift tube. The drift tube is kept under controlled conditions of pressure (2.3 mbar), temperature (60 °C) and voltage (600 V) resulting in a field density ratio (E/N) of ~ 125 Td (E being the electric field strength and N the gas number density; 1 Td = 10-17 V cm2). After a performed proton transfer reaction, protonated ions are extracted from the drift tube and pulsed every 30 μs to the orthogonal time- of-flight region to be separated according to their m/z ratio in the time-of-flight before being detected in conjunction with a multi- channel-plate (MCP) and a time-to-digital converter (TDC) (Burle Industries Inc., Lancaster, PA, USA). Ambient air was drawn with an external pump at a constant flowrate of ~27 l/min through a heated and coated PTFA Teflon inlet sampling line from the top of a micrometeorological tower located approximately in the middle of the four landfills.

PTR-TOF-MS data analysis

Raw 10 Hz time series of high resolved full mass spectra ranging from *m/z* 0 up to *m/z* 350 were continuously acquired by PTR-TOF-MS and stored in HDF5 file format in six-minutes time periods. After acquisition, each file was post-processed by the routine of a software designated for PTR-TOF-MS data analysis (Müller et al., 2013). The mass scale of all the recorded spectra was calibrated by exploiting four welled-fined PTR-TOF-MS background ion peaks (*m/z* = 21.022 , *m/z* = 39.0327 and *m/z* = 29.9974 corresponding to $H_3{}^{18}O^+$, and $H_2O\text{-}H_3{}^{18}O^+$, NO^+), and by inserting diiodobenzene (m/z = 203.948) continuously into the sample inlet. Despiking was performed on all post-processed ion signal intensities and a further reduction to hourly time resolution was carried out through a Matlab R2018a routine (The MathWorks Inc., Natick, MA, USA).

Determination of VOCs concentration

Theoretical absolute concentrations of VOCs were determined from PTR-TOF-MS measurements via the first order kinetic reaction (Lindinger et al., 1998). Cappellin et al. (2012) describe the correction for the effect of the duty cycle applied. The background signal of the PTR-TOF-MS was quantified via an automated system of switching valves that introduced VOC-free air, generated by a commercially synthetic air cylinder in which the humidity it was regenerated by a buffer between cylinder and sampling line, for 6 minutes every 6 hours and the resulting median value was subtracted from all the previously recorded data. Direct calibration of VOC was performed by measuring the signal intensities of a multi-component gas standard containing methanol, acetaldehyde, acetone, isoprene, methyl vinyl ketone, benzene, toluene, *trans*-2-hexenal, *cis*-3-hexenol, o-xylene and α-pinene (Apel Riemer, USA). All these VOCs were diluted through a commercially available multi-gas calibration unit by adding VOC-free air. In this study, concentrations are reported in $\mu g\ m^{-3}$ in order to compare them to the results reported in the section 3.1.1.

Qualitative analysis

July 23rd was selected as typical day in which estimate the representative burden of emitted VOCs in the summer period, in function of the higher daily average of temperature and radiation (Table 1). Highest values of temperature and radiation daily average, were also used to select 5th October as typical day for the autumn period (Table 2). As reported by Park et al. (2013), all protonated ions related to VOC and/or fragment of VOCs were recorded and then the major primary ions (e.g. H_3O^+, $H_2OH_3O^+$ $(H_2O)_2H_3O^+$), their isotopes (e.g. $H_3{}^{18}O^+$, $H_2{}^{16}OH_3{}^{18}O^+$), impurities such as $O_2{}^+$, NO^+, N_2H^+, ammonium ions (e.g. $NH_3{}^+$, $NH_3NH_3H^+$), and some artifact peaks surrounding the primary ion *m/z* ratios were excluded. Theoretical absolute concentration calculation routine was applied to the remaining peaks above *m/z* 31, by dividing each day in daytime and nighttime as a function of the hour of sunrise and sunset of each season. These protonated ions were categorized by their signal-to-noise ratios (S/N) and all ions above S/N=2 were classified in four groups by size. These groups include *m/z* ranges (i) from *m/z* 31 to *m/z* 69 (M31-69), (ii) from *m/z* 69 to *m/z* 136 (M69-136), (iii) from *m/z* 136 to *m/z* 237 (M136-237), and (iiii) from *m/z* 237 to *m/z* 350 (M237-350), following the classification used by Park et al. (2013). Individual concentrations of each VOCs were estimated as well as the cumulative concentration for each group and the total cumulative daytime and nighttime concentrations.

Results

Masses contribution to VOCs burden

In July, a total of 18 (~ 4,4%) and 27 (~ 6,2%) protonated ions above *m/z* 31 detected by PTR-TOF-MS passed the S/N=2 filter for daytime and nighttime, respectively In October, 29 (~ 7,4%) and 26 (~ 6,1%) protonated ions passed the S/N=2 filter for daytime and nighttime, respectively. Table 3 summarizes the number of protonated ions at each

July				October			
Daytime		Nighttime		Daytime		Nighttime	
Mass Groups	*n°*	Mass Groups	*n°*	Mass Groups	*n°*	Mass Groups	*n°*
Total masses	445	Total masses	434	Total masses	391	Total masses	425
S/N=2	18	S/N=2 filter	27	S/N=2 filter	29	S/N=2 filter	26
M31-69	11	M31-69	15	M31-69	12	M31-69	15
M69-136	7	M69-136	10	M69-136	9	M69-136	5
M136-237	0	M136-237	1	M136-237	5	M136-237	4
M237-350	0	M237-350	1	M237-350	3	M237-350	2

Table 3. Summary of the number of ions after each filtering step and in each *m/z* range group.

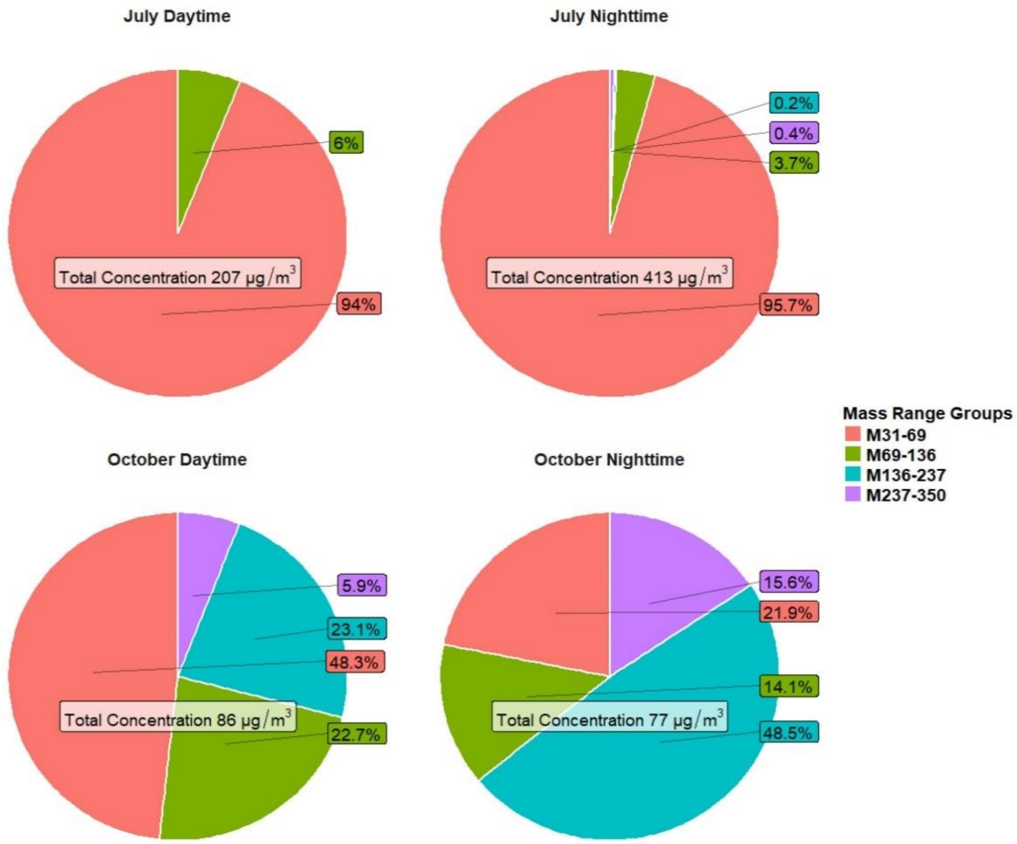

Figure 1. *m/z* range groups percentage contribution to total estimated concentrations of detected masses passed S/N=2, in Giugliano landfills site during daytime and nighttime in a typical day in July and October 2016.

filtering step of the qualitative analysis and the *m/z* range groups with their relative number of protonated ions. The percentages contribution of the *m/z* range groups to total concentration can be found in Fig. 1. Results show that M31-69 group (~ 95%) is the most representative range of masses in the burden of VOCs surrounding the four landfills for summer period in July, followed by M69-136, M136-237 and M237-350 groups. Daytime and nighttime show a similar contribution of the protonated ions groups to the total burden of VOC. For the typical day in October, the contribution of the mass range groups to the total estimated VOC concentration is more equally shared, but with different proportions among daytime and nighttime. M31-69 (48.3%) still is the mass group with the major contribution to the total estimated concentration during daytime, followed by M136-237, M69-136 and M237-350. Nighttime shows a major contribution of the M136-237 mass group (48.5%), with a decrease of the M31-69 and M69-136 mass groups contribution and an increase of the group with the higher range of masses (M237-350).

Real-time kinetics of VOCs concentration in air surrounding the landfills

Following the results of the punctual terrestrial measurements of VOC performed by Carriero et al (2018) on the same landfill site, we focused the attention on the concentrations of some important VOC in the landfill biogas. Some of these VOC are toxic or carcinogenic beside can be markers of aging and composition of the waste. We did not detect and estimate concentrations of chlorinated VOC because their proton affinity is below that of H_3O^+ and thus cannot be detected by PTR-TOF-MS (Spanel and Smith, 1999; Kennedy et al., 2003). On the other hand, we detected and showed concentration variations of some OVOC with a low *m/z* ratio and sulfur compounds, usually difficult to detect by sampling air in adsorption tubes following GC-MS analysis (Ciccioli et al., 2002). Real-time hourly concentration of OVOCs (acetic acid, methanol, formaldehyde, acrolein), arenes (toluene, benzene, xylenes), terpenes (monoterpenes and p-cymene), sulfur compounds (dimethyl sulfide and methylmercaptan) and other

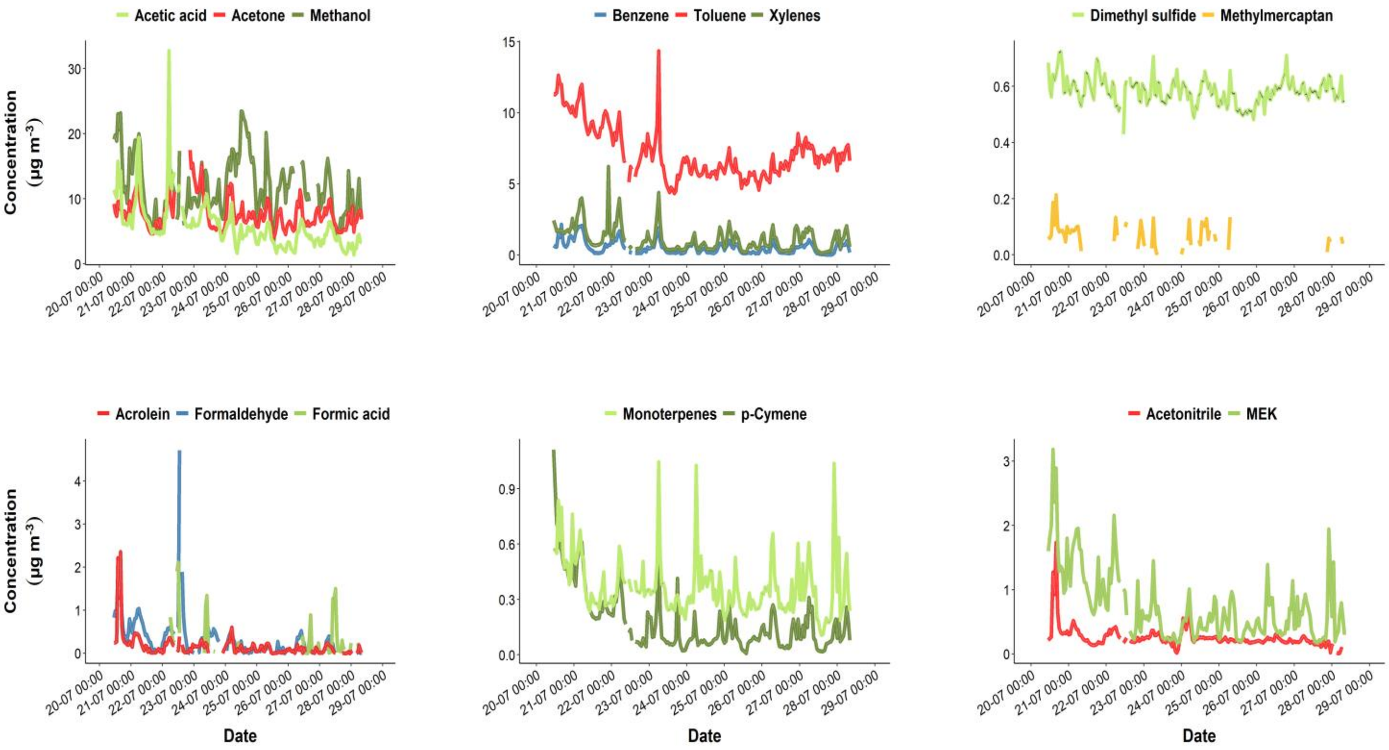

Figure 2. Hourly average concentrations of some "dominant" volatile organic compounds recorded from 20 to 28 July 2016 at Giugliano landfills site.

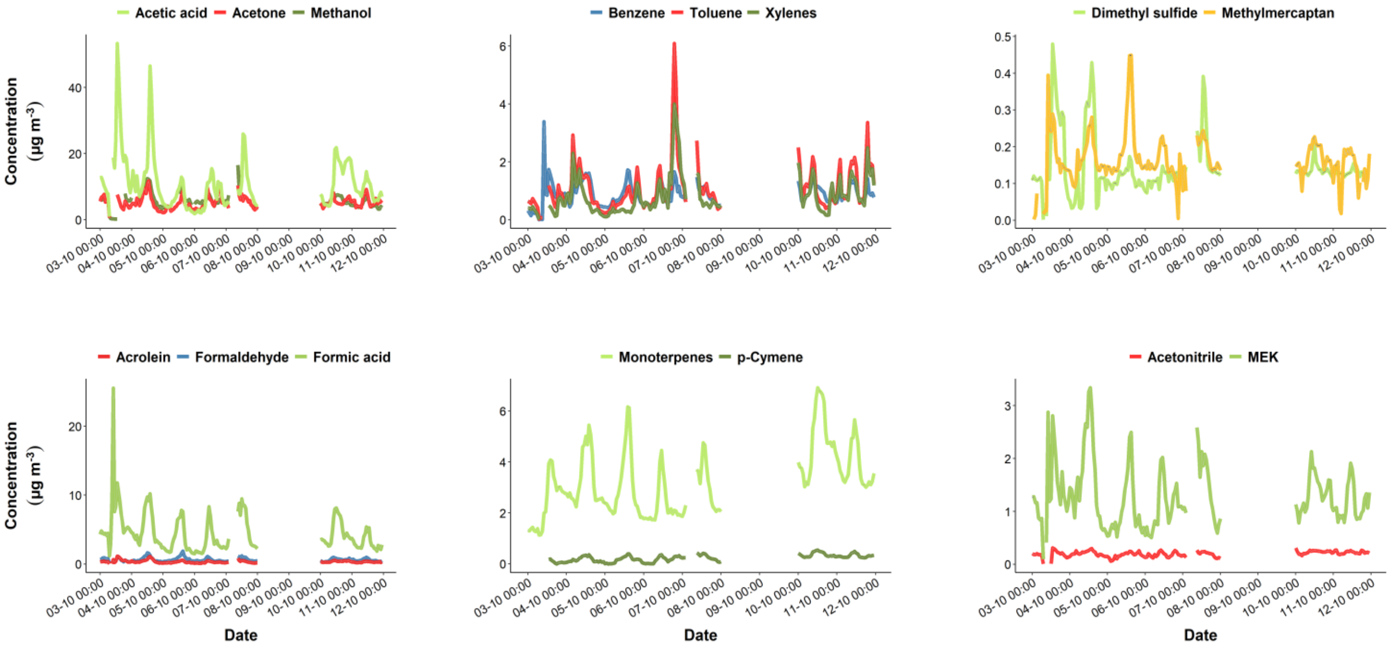

Figure 3. Hourly average concentrations of some "dominant" volatile organic compounds recorded from 03 to 11 October 2016 at Giugliano landfills site.

xenobiotic compounds (acetonitrile and MEK) monitored during the weeks in July and October are shown in Figure 2 and 3, respectively. Acetic acid dominated OVOCs, varying from 1.4 to 32 µg m^{-3} in July and from 0.9 to 53 µg m^{-3} in October. The second most abundant OVOC was methanol, varying from 3.5 to 23.4 µg m^{-3} and from 0.2 to 16.5 µg m^{-3} in July and October, respectively. Follow acetone (5.2 - 7.6 µg m^{-3}), formic acid (0.3 - 4.4 µg m^{-3}), formaldehyde (0.3 - 0.6 µg m^{-3}) and acrolein (0.15 - 0.34 µg m^{-3}). It needs to be highlighted the trend inversion of formic acid with higher maximum concentration in autumn (25.5 µg m^{-3}) than in summer (2 µg m^{-3}). Toluene dominated arenes contribution to the landfill biogas in July (4.3 - 14.3 µg m^{-3}), one order of magnitude higher of xylenes (0.13 - 6.2 µg m^{-3}) and benzene (0.02 - 2.14 µg m^{-3}). During the selected October week, the arenes contribution was lower than in the summer week, with toluene (0.02 - 6.2 µg m^{-3}) that still was the most abundant VOC, followed by xylenes (0.007 - 4 µg m^{-3}) and benzene (0.005 - 4 µg m^{-3}). Terpenes showed an inversion of this trend, with monoterpenes (1.13 - 7 µg m^{-3}) being one order of magnitude higher of p-cymene (0.0007 - 0.53 µg m^{-3}) in October. Among the sulfur compounds, only dimethyl sulfide and methylmercaptan were detected by PTR-TOF-MS from Giugliano landfills. These two sulfur compounds showed a similar concentration during the selected week in July and October, with a clearer daily cycle and higher concentrations of methylmercaptan in October (0.01 - 0.4 µg m^{-3}) than in July (0.0007 - 0.2 µg m^{-3}). MEK concentrations showed a similar trend to sulfur compounds, with a clear daily cycle in July (0.2 - 3.2 µg m^{-3}) and October (0.1 - 3.3 µg m^{-3}). A similar dynamics to MEK was recorded for acetonitrile, with quite higher concentrations in summer (0.01 - 1.7 µg m^{-3}) than in autumn (0.09 - 0.3 µg m^{-3}). In general, a clearer daily pattern of VOC concentration is shown in October than in July.

Discussion

The main focus of this paper was the PTR-TOF-MS employment for rapid and direct monitoring of VOCs concentrations in the air surrounding a landfill site. To our knowledge, this is the first study that investigates the qualitative VOCs burden into biogas and real-time concentration of VOCs in an illegally managed waste landfills. Other two studies have employed a real-time VOCs monitoring technology to investigate the waste material VOC emissions. However, a specific controlled process of anaerobic digestion of waste was monitored by PTR-TOF-MS (Papurello et al., 2012), or by a portable time-of-flight mass spectrometer in a municipal solid waste (Plocoste et al., 2017). This study has shown that major contribution to the total estimated concentration of detected protonated ions related to VOCs and/or fragments of VOCs is mostly made by M31-69 group in July. However, the percentage contribution of the groups to the total estimated concentration decreases, as well as the *m/z* range of the groups increases. These findings are supported by the concept that as the vapor pressure gets lower with the increasing chain molecular weight of VOCs and thus the relative importance of the evaporation becomes smaller for VOCs with higher masses. A similar trend to the typical day in July is shown in October for the daytime period, but with a higher contribution of the other groups of protonated ions related to VOCs and/or fragments of VOCs to the total burden of VOCs. During nighttime, the proportion of the mass groups contribution to the total VOCs concentration changes, and the M136-237 mass group has the largest estimated concentration. It is known that temperature is one of the major driver of volatilization and at with lower temperature values of the autumn, a mass groups contribution to the total concentration similar to summer is expected. However, this trend was not observed in autumn, especially during nighttime. Thus, the difference in the proportion of the groups contribution to the the total VOCs burden between July and October, could be explained by the seasonal variability of VOCs concentration with temperature and moisture, that cause a rapid biological degradation of organic matter (Zou et al., 2003; Chiriac et al., 2007). In fact, OVOCs like alcohols, aldehydes derive from waste biological fermentation (Staley et al., 2006, Scaglia et al., 2011), and these are the principal components of the lower mass groups during summer. OVOCs are the main components of the VOCs generated from the waste without aerobical pretreatment (Zhang et al., 2012). Not only high ambient temperature but also fermentation state is responsible for the higher OVOCs concentrations in summer and during daytime respect to nighttime (Duan et al., 2014). According to this, concentrations of OVOCs are higher during summer with a clear daily cycle, except for acetic acid and formic acid. Methanol is one of the most abundant OVOCs during summer and is probably related to the microbial alcohol formation from waste substrate (carbohydrate, starches, etc.) during the storage period under nearly anaerobic conditions at low pH (Staley et al., 2006). Indeed, alcohol and carbonyls acids are common intermediates of waste decomposition (Thomas and Barlaz, 1999). The inverse trend of acetic and formic acid with higher daily concentrations in the October can be supported by the study of Parker et al (2002) according to which carboxylic compounds may also come from the reaction between carboxylic acids and alcohols. Moreover, must be taken into consideration that a significant fraction of OVOCs come from a secondary production by the photochemical conversion of hydrocarbons (Jacob et al. 2002; Millet et al. 2004; Singh et al. 2000, 2004) affecting the OVOCs concentrations in remote areas. Arenes are toxic carcinogenic substance always present in the waste, mainly due to refuse composition of synthetic or hazardous materials (e.g., plastic packaging, plastic foam, solvents, and migrants from food containers) which emission is mainly related to volatilization process lead by temperature (Pierrucci et al., 2005; Staley et al., 2006, Duan et al, 2014). Data reported in this manuscript are in good agreement with other studies (Papurello et al., 2012; Duan et al., 2014), showing higher arenes concentration during daytime and that toluene dominates the aromatic compounds in the landfills, followed by xylenes and benzene. Indeed, toluene may come from direct volatilization of various sources, such as plastics, paper, and food containers (Kim et al., 2006; Parker et al., 2002) driven by temperature. In fact, as showed in Figure 1, toluene has a peak of concentrations on July 23rd, when the mean daily temperature reached the maximum in the week (Table 1). Benzene is a well-known carcinogenic compound and exposure to 1 $\mu g/m^{-3}$ produces a lifetime risk of 4×10^{-6} for leukaemia. Usually, 5 $\mu g\ /m^{-3}$ is considered as a practical limit (EEA, 2008). In contrast to some reports in the literature, in this study the levels of benzene were under the EEA limit. Terpenes are significant odor-causing compounds in landfills and may play an important role in the perception of waste odor in combination with certain microbial volatiles (Statheropoulos et al., 2005). Among them, D-limonene is widely considered indicator of fresh waste (Sadowska-Rociek et al., 2009) emitted in the initial decomposition stage (Komilis et al., 2004; Pierucci et al., 2005). Our results seem to be in contrast with those of Carriero et al (2018) recorded on the same landfill site, where high p-cymene content were reported consistently with relative low limonene concentration. In fact, the results of this study show higher concentrations of monoterpenes than p-cymene, especially in the October week. P-cymene is reported to originate from the microbial transformation of monoterpenes, such as limonene, and high content can be taken as an indication of a prolonged anaerobic waste degradation (Davoli et al., 2003). However, this discrepancy is explained by the inability to estimate with PTR-TOF-MS the proportion between the several isomers of terpenes (α-pinene, β-pinene, camphene and limonene) that are detected together on the same mass peak according to Riemer et al. (1994).. A clear daily cycle driven by temperature is shown in October, less pronounced during the summer week. This could be explained by the great potential of SOAs and ozone production (Hoffmann et al., 1997) of monoterpenes and p-cymene by photo-oxidation lead by temperature and light (Fehsenfeld et al., 1992; Atkinson & Arey, 2003; 2012; Calfapietra et al., 2013), since climatic conditions favor photochemical processes during summertime in the Mediterranean area (Fountoukis et al., 2011). Interestingly, the presence of sulfur compounds were not reported by Carriero et al (2018) on the same site thatused a different technique to sample and analysie VOC. Along with monoterpenes and p-cymene, sulfur compounds are commonly known odor-causing pollutants in landfills (Muezzinoglu, 2003). Sulfurated compounds can be naturally present in food as aroma or originate when food decay process starts (Kim et al., 2009; Landaud et al., 2008). Food sulfur content in waste volatilizes during fermentation and is released into the atmosphere (Wu et al., 2010). Then, sulfur compounds production is mainly due by microbial activities during aerobic decomposition. In this study, dimethyl sulfide was more abundant in summer than in autumn, and it showed similar magnitude and daily trend than methylmercaptan. The increase of methylmercaptan concentration and the well-defined daily cycle in October could be attributed to different waste decomposition state and photochemical reactions occurring in the atmosphere (Duan et al., 2014). Studies on the oxidation pathways formation of sulfur compounds under photochemical conditions in landfills reported the transformation of oxidized pollutants when combined with ozone, nitrogen oxides, and other substances (Shon et al., 2005; Song et al., 2007). These sulfur compounds may undergo a certain degree of transformation in landfill air during summer. The high relative concentrations of MEK (2-butanone) is in line with the findings of Carriero et al., (2018) on the landfills of the same area. Indeed, along with arenes, MEK can originate from dumping of solvents used in industrial processes (gums, resins, cellulose acetate, and cellulose nitrate production) in the landfill. On the other hand, MEK could derive also from extensive biochemical waste degradation. Measuring VOCs concentration directly in the air surrounding the same landfills where Carriero et al. (2018) found MEK, we can support the hypothesis that MEK originates from industrial solvents illegally dumped. The last interesting VOC to analyze is acetonitrile, rarely reported in landfills emissions because the difficulty in detection with standard analytical technique. Consistent with the findings of Gallego et al (2014) this nitric compound is always present in very low concentrations in landfills, often below the limit of detection. Finally, we are aware that fluxes calculation would have produced much better results to support the interpretation of sources and possible sinks of VOC at the site. Especially having a PTR-TOF-MS deployed at landfill site coupled with EC system. However, because this work is in preparation, fluxes calculation is still work in progress.

Conclusions

In this study, for the first time we employed the PTR-TOF-MS to estimate all the protonated ions related to VOCs and/or fragment of VOCs detected in the air surrounding an illegally managed waste landfill. Moreover, we characterized real-time concentrations of important VOCs belonging to several classes (OVOCs, arenes, terpenes, sulfur compounds). All protonated ions were subdivided into four groups of range of masses and the contribution to the total VOC concentration in two season was estimated. The group with the lower range of masses (M31-69) was found to give the major contribution to the total VOCs burden in July, but this trend changed in October. This trend inversion is probably due to the enhanced production of OVOC during summer, which are the principal components of the group of lower masses. In fact, OVOC are mainly emitted in summer showing a clear daily cycle lead by temperature, with methanol being among the most abundant VOC probably originated from microbial alcohol formation in waste degradation. Conversely, acetic and formic acid are more abundant in autumn, probably related to the secondary production due the reaction among carboxylic acids and alcohols and hydrocarbons photochemical conversion. Arenes are dominated by toluene and characterized by higher concentrations during daytime, originating by direct volatilization from xenobiotic materials like plastics and solvents, lead by temperature. Benzene showed concentrations always below the EEA limit of 5 μg /m^{-3}. Terpenes along with sulfur compounds are well known odor-causing compounds in landfills, both most abundant in autumn probably because they undergo a certain degree of photo-oxidation lead by temperature and light in summer. Fluctuations of MEK concentrations are in the same order of magnitude in both season, originating from illegally dumped solvents along with arenes. Acetonitrile, rarely reported in landfill VOCs emissions, was found in low concentrations, consistent with the literature. Summing up all these results, it can be concluded that VOCs composition and concentration variations are highly related with seasonality, waste degradation state, temperature and radiation, especially in the summer. Higher temperature and moisture content in summer tends to cause rapid biological degradation of organic matter and production of relatively large volume of biogas within landfill, whereas photo-oxidation and secondary production occur. These results denote that in this landfill site, vehicles activity does not significatively affect arenes concentrations. This work provides important information about the composition and real-time concentrations variation of VOCs present in landfill biogas.

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3.2. (2nd study case). “Exchange of BVOCs by an agricultural ecosystem in the Mediterranean area”

3.2.1. Biogenic Volatile Organic Compounds (BVOCs) exchanges from *Sorghum bicolor L.* during a whole growing season in Southern Europe. Manco et al. (in preparation)

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Abstract

Plants emit significant amounts of biogenic volatile organic compounds (BVOCs), which affect air quality and regional climate. BVOCs exchanges are related to plant species and environmental factors, such as temperature, light radiation and water availability. Since *Sorghum bicolor L.* (sorghum) is becoming an increasingly valid alternative to maize in Southern Europe as well as in most non-irrigated region with limited precipitation, it is important to investigate the BVOCs exchanged from this crop. Up to now, only few studies have measured BVOCs exchanges at ecosystem scale over an entire growing season; in particular, no study have investigated flux emission from crops grown in the Mediterranean area. Here we report, for the first time, BVOCs fluxes measured at ecosystem scale and from over a whole growing season in sorghum field located in Southern Europe. By using real-time detection of BVOCs concentrations measured with Proton Transfer Reaction ‘Time-of-flight’ Mass Spectrometer (PTR-TOF-MS) and Eddy

Covariance technique, we calculated the BVOCs exchanged for about 3 months. Oxygenated-BVOCs (OVOCs) were mainly exchanged. Methanol was the most abundant BVOC to be emitted with a total average emission rate of 0.14 ± 0.013 nmol m^{-2} s^{-1}, followed by acetaldehyde (0.07 ± 0.004 nmol m^{-2} s^{-1}). Other OVOCs like formaldehyde acetone, acetic acid, formic acid, MVK/MAC, were emitted and deposited in different extent during sorghum growth. Monoterpenes were poorly exchanged and mainly depsosited, with an average deposition rate of -0.0001 ± 0.0003 nmol m^{-2} s^{-1} over the whole growing season. Green leaf volatiles (GLVs) showed emissions burst following the occurrence of mechanical stress events. Indeed, methanol, acetaldehyde, acetone, formic acid and GLVs showed to be related to cutting and lodging events occurred during sorghum growth. Our results show different BVOCs dynamics as a function of synergistic interrelationship among plant growth, environmental parameters and occurring stresses. The exchanges of BVOCs from sorghum are similar to those observed on other crops (mainly maize) for some BVOCs (such as methanol, acetaldehyde, acetone), instead for other BVOCs (such as acetic acid, monoterpenes, toluene) they seem to be different, revealing a variability related to species and world region.

Introduction

Agricultural areas cover ~35% of the Earth land surface (FAO, 2016). For the need to sustain the growing world’s human population with food and energy will likely be necessary to convert part of the actual natural grasslands and forests to new agricultural land by 2050. Vegetative ecosystems emit large amounts of volatile organic compounds (VOCs) estimated to be ~760 Tg C per year, which largely exceed those from anthropogenic, sources (Sinderalova et al., 2014). Composition and exchange dynamics of VOCs emitted from biogenic surces (BVOCs) strongly depend on plant species and environmental factors such as temperature, radiation intensity and water availability (Kesselmeier & Staudt, 1999). Most of the BVOCs are very reactive within the atmosphere and participate to the formation of secondary organic aerosols (SOAs), as well as to photochemical ozone production (Atkinson & Arey, 2003; Ashworth et al., 2012; Makkonen et al., 2012; Schultz et al., 2015), thus affecting air quality and climate at regional level (Rosenkranz et al., 2015). For several years, forests have been the most widely studied ecosystem concerning BVOCs emissions (Niinemets et al., 2013). Indeed, up to now, only few studies have measured BVOCs exchange in croplands (Warneke et al., 2002; Karl et al., 2005; Eller et al., 2011; Copeland et al., 2012; Crespo et al., 2013). In particular, in Europe, BVOCs emissions have been widely investigated only in short rotation coppices (SRC) of poplars (Ashworth et al., 2013; Brilli et al., 2016, Portillo-Estrada., 2018). Moreover, an ever-smaller number of studies focused on maize, often providing measurements that spanned for short time periods during the early growth stages (Das et al., 2003; Graus et al., 2013; Leppik et al., 2014). Recently, only two studies have monitored fluxes of BVOCs from maize over an entiregrowing season and they mainly reported fluxes of methanol, acetone, acetaldehyde, acetic acid, monoterpenes (MTs) and green leaf volatiles (GLVs) (Bachy et al., 2016; Wiß et al., 2018). Previous research has documented that across Europe, by maintaining current genotypes, sowing dates, and the mix of rainfed and irrigated land use would result in a 20% decrease of maize yields by 2050 due to the climate change (Webber et al., 2018). Therefore, the replacement of maize with alternative, drought and heat resistant crops is needed. Grain sorghum (*Sorghum bicolor L.*) is a forage species and a valid alternative crop to maize for animal feed in Southern European regions, as well as in any non-irrigated area characterized by very limited precipitation, especially in summertime (Balole & Legwaila, 2006). Past laboratory experiments simulating leaf-drying/senescence have shown Sorghum can be a source of acetaldehyde along with methanol and other oxygenated BVOCs (Karl et al., 2005). In this study, for the first time, we measured at ecosystem-scale fluxes of BVOCs in a sorghum crop cultivated in Southern Italy during the whole growing season. In particular, we investigated the synergic effect of environmental factors and crop phenological stages on emission and deposition of BVOCs. Our objectives were: to (i) quantify e the BVOCs flux exchanges during all phenological stages of the crop; (ii) evaluate the impact of environmental variables and phenology on dynamics and source strength of BVOCs; (iii) characterize the BVOCs profile of stress events (i.e. cutting and lodging) occurring during the growing season.

Material and Method

The experimental site

Measurements were carried out from 1st of June to 9th of September 2018 in a farm located in Southern Italy (IT-Bci, Borgo Cioffi, Eboli, Italy; latitude 40° 31′ 25.5″, longitude 14° 57′ 26.8″; mean altitude 15 m a.s.l), which is an experimental station candidate to ICOS (Integrated Carbon Observation System) network of permanent sites (www.icos-ri.eu). Because of the heterogeneity of the canopy due to spots cuts in the field, we considered measurements until August 23th for fluxes computation. The area under study is characterized by a typical Mediterranean climate with hot and dry summer and cool rainy winter. The area of the experimental field is 10 ha, whereas the footprint along the prevalent wind direction (NE-SW) is 200-250 m (Vitale et al., 2016). Soil texture is silt-clay; parent soil material is calcium carbonate, but most of the material has an alluvial origin, deriving from nearby Sele River. Vitale et al. (2009) shows further details on soil characteristics. Sorghum (*Sorghum bicolor x Sorghum sudangrass*., cv. Nicol, Pioneer) was sown on 17th of June at row spacing of 5 cm and inter-row spacing of 15 cm, with a nominal sowing density of 70 kg/h and ~ 200 plants m^2 after emergence. Plants emerged on 24th of June and were harvested on 9th until 15th of August. From the 1st of June to the sowing date operation of plowing and ripping were carried out. Irrigation was delivered by a central pivot system.

PTR-TOF-MS set-up

A Proton Transfer Reaction "Time-of-Flight" Mass Spectrometer (PTR–TOF 1000, Ionicon, Innsbruck, Austria) described by Graus et al. (2010) was employed to monitor concentration of a wide range of BVOCs. BVOCs were detected in real-time through proton transfer reactions that take place among H_3O^+ ions produced within the ion source and the sample gas inserted into the PTR-TOF-MS drift tube. The drift tube was kept under controlled conditions of pressure (2.24 mbar), temperature (80°C) and voltage (520 V) resulting in a protonation energy (E/N) of ~122 Td (E being the electric field strength and N the gas number density; 1 Td=10^{-17} V cm^2). After performing proton transfer reaction, protonated ions related to BVOCs and/or fragment of BVOCs were extracted every 30 ms from the drift tube and then pulsed to the orthogonal time-of-flight region to be separated according to their *m/z* ratio before being detected with a multi- channel-plate (MCP) and a time-to-digital converter (TDC) (Burle Industries Inc., Lancaster, PA, USA). Instrumental background signals were automatically measured for 6 minutes 2-4 times per day via a multiport valve that switched the inlet flow from ambient air to BVOC-free air, produced by a catalytic converter (ZA FID AIR 1,5 L; LNI Swissgas Srl).

PTR-TOF-MS data analysis

PTR-TOF raw data were continuously acquired and stored in HDF5 file format every 6 minutes (http://www.hdfgroup.org/); then each file was post-processed through the PTR-TOF Data Analyzer software (Müller et al., 2013). This software performs: a) a careful mass scale calibration and peak detection, b) peak shape analysis, c) iterative residual peak analysis for the multiple isobaric peaks detection per unit m/z, d) fitting of the peak areas quantification corresponding to ion signal intensities based on the 6-min sum spectra. Calibration of the mass scale of all recorded spectra was made both by

m/z	Molecular Formula	Likely compound	Isotope[a]	Fragments[a]
21.022	$H_3{}^{18}O^+$	Hydronium ion		
31.018	$CH_2O\text{-}H^+$	Formaldehyde (FORM)		
33.034	$CH_3OH\text{-}H^+$	Methanol		
39.0327	$H_3O(H_2{}^{18}O)^+$	First Water Cluster Isotope		
42.033	$C_2H_3N\text{-}H^+$	Acetonitrile		
45.034	$C_2H_3OH\text{-}H^+$	Acetaldehyde		
47.013	$CH_2O_2\text{-}H^+$	Formic acid (FA)		
59.049	$C_3H_6O\text{-}H^+$	Acetone/Propanal	60.053	
61.029	$C_2H_4O_2\text{-}H^+$	Acetic acid		
69.069	$C_5H_8\text{-}H^+$	Isoprene/Pentenols/Methylbutanals fragment	70.075	
71.049	$C_4H_6O\text{-}H^+$	Methyl vinyl ketone (MVK)/Methacrolein (MAC)		
75.043	$C_3H_6O_2\text{-}H^+$	Propionic acid		
79.054	$C_6H_6\text{-}H^+$	Benzene		
85.065	$C_5H_8O\text{-}H^+$	Pentenal		
87.084	$C_5H_{10}O\text{-}H^+$	Pentanal/Methylbutanals/Pentenols		
93.069	$C_7H_9\text{-}H^+$	Toluene		
99.080	$C_6H_{10}O\text{-}H^+$	*trans*-2-Hexenal		43.018 81.07[b]
101.096	$C_6H_{12}O\text{-}H^+$	*cis*-3-Hexenol		83.08
107.086	$C_8H_{10}\text{-}H^+$	Xylenes		
111.118	$C_8H_{14}\text{-}H^+$	Octyne/Cyclooctene		
113.058	$C_6H_8O_2\text{-}H^+$	Hydroxy-methyl-cyclopentenone/Dimethyl-Furanone		
135.121	$C_{10}H_{14}\text{-}H^+$	*p*-Cymene		
137.133	$C_{10}H_{16}\text{-}H^+$	Monoterpenes (MT)		81.07
149.094	$C_{10}H_{12}O\text{-}H^+$	Methyl-chavicol		
155.137	$C_{10}H_{18}O\text{-}H^+$	Linalool/Eucalyptol		

Table 1. Selected relevant ion exchanged during sorghum growing season. Molecular formula, possible compound, exact mass *(m/z*) of the parent ion mass peak, isotopes and fragments.

[a] Signals of detected isotopes and fragments were summed to parent ions

[b] For *m/z* 81.07 we measured fragmentation rate of *m/z* 137.133 and then we back-calculated the proportion of *m/z 99.08*

exploiting three well-defined PTR-TOF-MS background ion peaks (m/z=21.0221, m/z= 29.9974 and m/z= 39.0327 corresponding to $H_3{}^{18}O^+$, NO^+ and H_2O-$H_3{}^{18}O^+$, respectively), and diiodobenzene (m/z = 203.948) continuously inserted into the sample inlet. Background average subtraction, fragments correction, theoretical concentration calculation and despiking were performed on all the post-processed high frequency protonated ion signal intensities through a custom made Matlab R2018b routine (The MathWorks Inc., Natick, MA, USA), programmed by myself for VOCs data processing. Among all the peaks detected by PTR-TOF-MS related to protonated ions within the selected mass range, in this work we focused on 23 relevant protonated ions (Table 1) related to sorghum growth at site, selected on the basis of the most relevant ones which have been reported in four previous studies where BVOCs fluxes have been measured from grasslands and cropland (Ruuskanen et al., 2011; Park et al., 2013; Bachy et al., 2016; Wiß et al., 2018).

Determination of BVOCs concentration

From PTR-TOF-MS measurements, theoretical absolute concentrations of BVOCs were calculated by applying the first order kinetic reaction (Lindinger et al., 1998) after the correction for the effect of the duty cycle as proposed by Cappellin et al. (2012)

$$[VOC]_{VMR} = \left(\frac{1}{k\tau}\right) \times \left(\frac{[VOCH^+]measured}{[H_3O^+]measured}\right) \times \left(\frac{\sqrt{\left(\frac{m}{z}\right)H_3O^+}}{\sqrt{\left(\frac{m}{z}\right)VOCH^+}}\right)$$

where [VOC-H^+] and [H_3O^+] are signal ion rates corresponding to the protonated VOC-ions and the primary ion, respectively; τ is the reaction time of [H_3O^+] in the drift tube (de Gouw et al., 2003; Tani et al., 2003); *k* is the reaction rate coefficient between VOCs and H_3O^+ according to the values provided by Cappellin et al. (2012). When *k* was not available, a standard value of $2*10^{-9}$ cm^3 s^{-1} was used. The [$H_3{}^{16}O^+$] concentration at m/z

= 19.018 was calculated from the natural isotope [$H_3{}^{18}O^+$] measured at m/z = 21.022. Limits of detection (LOD) were calculated according to LOD = 2 * standard deviation$_{\text{background}}$/sensitivity (Karl et al., 2007). In addition, direct calibration of the PTR-TOF sensitivity was performed during the campaign, by measuring the signal intensities of a multi-component gas standard (Apel Riemer, USA) containing: methanol (*m/z* 33.033), acetaldehyde (*m/z* 45.034), acetone (*m/z* 59.049), isoprene (*m/z* 69.069), methyl vinyl ketone (*m/z* 71.049), benzene (m/z 79.054), toluene (*m/z* 93,069), *trans*-2-hexenal (*m/z* 99.0819), *cis*-3-hexenol (*m/z* 101.096), o-xylene (*m/z* 107.081) and α- pinene (*m/z* 137.133) at nominal concentration of 1 ppmv each. In order to achieve various concentrations of VOCs in the low ppb range (5-50 ppb), we used a multi-gas calibration system (Environics Series 6100, Environics, Tolland, CT, USA) to diluting the gas standard with VOC-free air having the same relative humidity than the ambient air.

BVOCs flux measurements

BVOCs fluxes were calculated through the Eddy Covariance technique (Aubinet et al., 2000). A system including a 3-D sonic anemometer (R3-100, Gill Instruments Limited, Hampshire, UK) coupled with PTR-TOF was set up to measure volume mixing ratios (VMRs) of BVOCs in combination with wind velocity and speed at high frequency. Data streams from PTR-TOF-MS and anemometer were independently acquired by two different computers and synchronized with a specific software (NTP, Network Time Protocol, University of Delaware, DE, USA) to an independent external clock through the Internet, with an accuracy <20 ms. Sonic anemometer and the other gas analyzers (shown below) were mounted on a 2.30 m high mast. In order to have a reliable aerodynamic measurement height during the sorghum growth, the entire mast was raised to 3.05 m high from the 1st of August, 2018. In order to maintain a Reynolds number >6000, ambient air was drawn with an external pump at a constant flow rate of ~28 sl min^{-1} (standard liter per minute; air volume normalized to standard temperature and pressure conditions: 273 K, 101.3 kPa) into a PFA Teflon sampling line ~ 35 m long with an inner diameter of 12 mm before to be sampled by the PTR-TOF-MS. To avoid water vapor condensation inside the sampling line, and thus prevent partial dissolution of BVOCs in the water film, the sampling line was thermally insulated and heated (~ 40 °C). A PTFE filter (Savillex, 37 mm diameter, 5-6 micron pore size) was installed 0.55m downstream of the sampling line in order to keep the tube clean from air dust. The last meter of the sampling line was converted first from 1/2' to 1/8’ and then from 1/8’ to 1/16’ to match the capillary inlet of the PTR–TOF–MS system, that drawn a subsample of the air flow (~ 0.25 sl min^{-1}). In this paper, fluxes are expressed per m^2 of soil and a positive flux indicates an emission from the ecosystem to the atmosphere, wherease a negative flux indicates a deposition from the atmosphere to ecosystem.

BVOCs flux calculation

For BVOC fluxes computation with the Eddy Covariance method of the BVOCs concentrations, a customized version of EddyPro (www.licor.com/eddypro, Fratini et al., 2012) named EddyVoc, was employed. EddyVoc processing routine in a first step hide raw data with a quality flag, excluding individual spikes and values out-of-range (such as negative concentration values). Subsequently, the software performs two-component axis rotation for tilt correction (Wilczak et al., 2001), linear de-trending (Rannik and Vesala, 1999) and time-lag estimation based on the covariance maximization (Aubinet et al., 2000). A first run using the 2.5-5.5 s lag-time window was performed to search for the absolute maximum value in the cross-covariance function, followed by a second run using a constant time-lag extrapolated on the basis of the first analysis. With this information about time-lag, it is possible to choose either fluxes estimated with constant time-lag or using maximization of covariance for final processing. The detailed approach explaining the time-lag calculation is described by Taipale et al. (2010) and Langford et al. (2015). Because methanol showed the strongest signal-to-noise ratio during the measurements period, it was used to compute the constant 30-min time-lag for all other compounds, with assumption that all BVOCs were affected by the same physical turbulent transport in the sampling line (Fares et al., 2012). The time-lag found for methanol was 5 s, close to the time-lag experimentally determined in situ by methanol (4 s) and acetone (5 s) injection. Corrections for flux losses were also applied as well as for sensor separation (Horst and Lenschow, 2009) and low pass frequency (Moncrieff et al., 2004). High frequency spectral correction was performed according to the model of Ibrom et al. (2007), using methanol for the spectral assessment estimation that was applied applied to all VOCs.

Quality control and random uncertainty determination

Half-hourly fluxes quality control were applied following Göckede et al. (2004), assigning quality flag (0 for good data, 1 for acceptable data, 2 for bad data) to each flux value. We did not apply friction velocity filter, following the same approach of Bachy et al. (2016) based on the assumption that u_* can actually control soluble BVOCs fluxes (Aubinet et al., 2012; Laffineur et al., 2012). For each individual 30-min flux, random uncertainty was estimated as the standard deviation σ of the covariance function for a time lag window far from the theoretical time lag and therefore physically irrelevant (Wienhold et al., 1995; Spirig et al., 2005). Multiplying random error for α (α =1.96 for the 95th percentile; α =3 for the 99th percentile) gives limit of detection (LoD) of the fluxes (Langford et al., 2015). Varying among the compounds, 31 to 9 % of the fluxes were above the detection limit (using α =1.96). Because many fluxes were below their detection limit, half-hourly fluxes were very scattered around zero, except for methanol during the final period of the growing season. For this reason, we averaged fluxes over larger observation periods, typically the whole growing season, weeks and phenological stages. Both fluxes estimated with constant time-lag and maximization of covariance do not show significant differences to exceed LoD in the first period of the growing season (data not shown), where fluxes are always scattered around zero, also averaging over larger periods. Thus, we used fluxes estimated with maximization of covariance, because it is not introducing bias in the last part of the measurements where fluxes are not scattering around zero and constant time-lag probably underestimate fluxes.

Other ancillary measurements

Simultaneously to BVOCs, CO_2 and H_2O fluxes were measured by using the conventional eddy covariance technique, by coupling the same sonic anemometer used to measure BVOCs fluxes with a closed-path infrared gas analyzer (IRGA, Li-7200, LI-COR, Lincoln, NE, USA). In addition, meteorological data were recorded above the canopy: photosynthetic photon flux density (PPFD) by (Li-190; LI-COR, Lincoln, NE, USA), air temperature (T) and relative humidity (RH) (CS215-L; Campbell Scientific, Logan UT, USA). The site was also equipped with a rain gage (TE525-L; Campbell Scientific, Logan UT, USA) to measure precipitations and a barometric pressure transducer (Setra 278; Setra System Inc., Boxborough MA, USA) to measure air pressure. Sorghum phenology was monitored though daily pictures taken with a phenological camera (HBD3PR1; Honeywell, Austin, TX, USA). The leaf area index (LAI) and aboveground biomass were measured at the beginning, mid and end of the measurement period, by destructive sampling of 1 m^2 of vegetation with six replicates. LAI was estimated by detaching leaves and measuring their surface using an area meter. Biomass was determined gravimetrically by separately oven drying to constant weight the different plant parts (Vitale et al., 2010).

Results

Sorghum phenological development

According to the Sorghum Growth and Development, Texas Cooperative Extension (Gerik, Bean & Vanderlip, 2003), the sorghum-growing season was divided into four phenological phases: GS0 (sowing and germination); GS1 (leaf unfolding); GS2 (panicle emergence); GS3 (flowering). The field was considered almost completely as bare soil in the stage GS0 and the sorghum developed during the following stages. Vegetative growth characterized stage GS1, whereas grain initiation and flowering occurred during stages GS2 and GS3. Sorghum for silage is typically harvested at the soft dough stage, in

Growth Stage	Date	Approximate days after emergence	AGB [Kg m^{-2}]	GAI [m^{2} m^{-2}]	Description of sorghum development
GS0	1 June–3 July	0-9	0	0	Before sowing to 3-leaf stage Emergence on 24 June Considered bare soil during all the stage because of the small biomass
GS1	4-26 July	10-20	0.222	6.800	From 3-leaf stage to 5-leaf stage
GS2	27 July-17 August	32-52	0.744	17.298	From panicle initiation to heading stage Important increase in leaf area index Starting of the harvesting for ensilage in the final part
GS3	18-21 August	53-56	1.491	12.980	From flowering to soft dough stage Continue of the harvesting for ensilage

Table 2. Sorghum phenological development. Growth stages refer to Sorghum growth and development, Texas Cooperative Extension – Gerik, Bean & Vanderlip (2003).

the middle of the phase GS3. For this reason, the senescence was not included in the phenological description. Phenological stages, development and dates are summarized in Table 2.

Meteorological, physiological and phenological data

Meterorological, physiological and phenological conditions at the field site are summurized in Figure 1. GAI (Green Area Index) reached his maximum of 17.2 ± 1.7 m^{2} m^{-2} at stage GS2. Garofalo et al (2011) reported a maximum GAI of 8.2 m^{2} m^{-2} for sorghum grown in Mediterranean area. Chaochen et al (2017) showed as GAI increases as plant density increases. This would explain the high GAI reported in this study, with a density of ~ 200 plants m^{-2}. Above ground biomass (AGB) reached his maximum (1.5 ± 0.31 kg m^{-2}) at the beginning of the stage GS3. Net CO_2 ecosystem exchange (NEE) was positive throught the GS0 stage according to the absence of photosyntetic CO_2 assimilation by plants. The onset of net CO_2 uptake began in stage GS1, when sorghum starts the

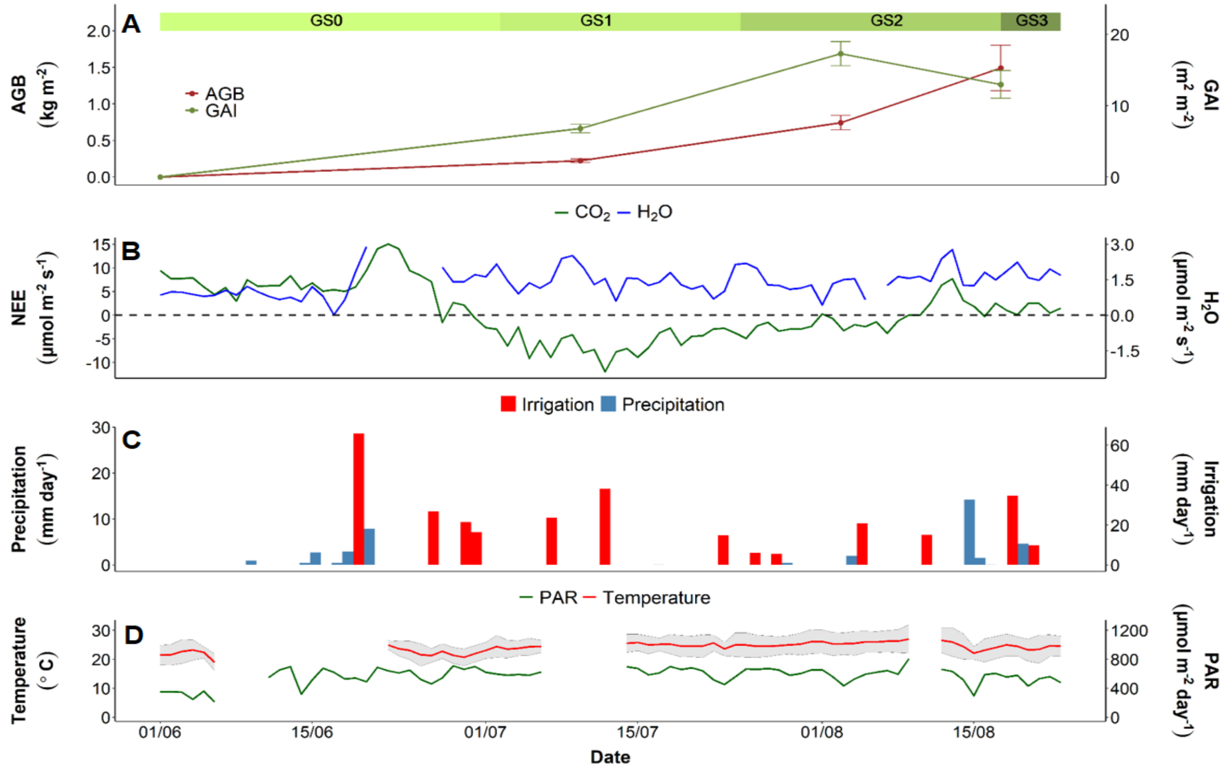

Fig. 1 Meteorological, physiological and phenological of sorghum recorded from 1 June to 23 August 2018. From the top to the bottom: A) phenological stages, above ground biomass (AGB) and green area index (GAI); B) net ecosystem exchange of CO_2 (NEE) and H_2O evapotranspiration; C) precipitation and irrigation; D) temperature and photosynthetically active radiation (PAR).Temperature (N=48, means +/- SE), radiation, NEE, and H_2O are shown as daily averages, while precipitation as daily sum.

vegetative growth. A change in NEE was observed in the middle of the GS2 stage with a consistent uptake followed by a net emission of CO_2 in the final part of the measurements. Water flux (H_2O) was positive through all the sorghum growth, showing a quite costant pattern and order of magnitude during all the stages. The sorghum growing season was characterized by occasional rainy events and quite constant irrigation, high daily mean temperature (~25 °C) and maximum incoming PAR almost always below 700 µmol m^{-2} day.

BVOCs exchange from sorghum during the growing season

Throughout the study period, methanol was the main BVOCs emitted from the sorgum field with an average emission of 0.14 nmol m^2 s^{-1} and a maximum rate of 0.6 nmol m^2 s^{-1} during the GS3 phase (Fig. 2). Emissions of methanol were observed in the stage GS2-GS3, whereas deposition occurred during the first two stages GS0 and GS1. Other OVOCs, like acetone, acetaldehyde, acetic acid, formic acid, MVK/MAC, formaldehyde where also emitted and/or deposited in different extent through the phenological stages. Acetaldehyde was the second most emitted BVOC, with an average emission of 0.07 ± 0.004 nmol m^2 s^{-1} during the whole growing season and a maximum rate of 0.19 ± 0.1 nmol m^2 s^{-1} during the GS2 phase.

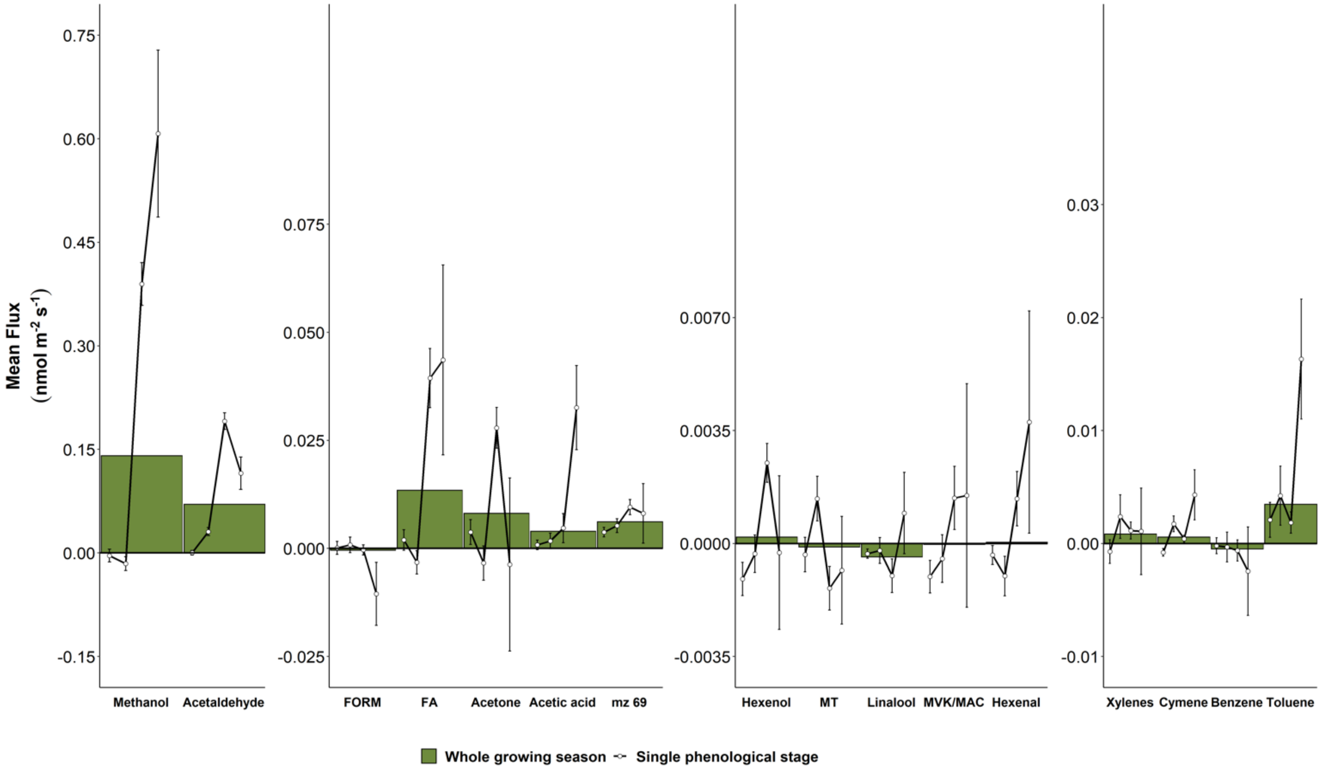

Fig. 2 BVOCs exchanges over the whole growing season. Points are the average fluxes (± standard error) of each phenological stage. Bars represent the total average fluxes of each BVOC during the whole growing season. Phenological stages from left to right: GS0, GS1, GS2, GS3. See Table 1 for BVOC abbreviations and Table 2 for phenological stage description.

Formic acid and acetone also resulted emitted during the growing season (0.013 ± 0.002 and 0.008 ± 0.002 nmol m^2 s^{-1}, respectively), but with fluxes that were both emitted and deposited and varied magnitude through the phenological stages. Acetic acid also resulted to beemitted (average value of 0.004 ± 0.001 nmol m^2 s^{-1}) through all the phenological stages, with a maximum of 0.032 ± 0.02 nmol m^2 s^{-1} in stage GS3. To a lesser extent, other OVOCs were exchanged, like formaldehyde and MVK/MAC. The *m/z* 69 signal showed an emission increase during the developing stages of the crop, following the small increase of PAR in the first phenological stage and the small decrease during last stage (Fig. 1). The *m/z* 69 is commonly associated with isoprene in PTR-MS BVOCs studies, but this signal can also derives from proton transfer reaction of other BVOCs. However, through the study we did not observed any correlation of *m/z* 69 with temperature and PAR and then we are not able to state that these emissions originate from isoprene. The *m/z* 69 exchanges were 2 order of magnitude smaller than the methanol exchanges, with a maximum emission of 0.009 ± 0.003 nmol m^2 s^{-1} during stage GS2. Monoterpenes were deposited during the whole season, except for a small emission (0.001 ± 0.0008 nmol m^2 s^{-1}) in phase GS1, resulting in a total average of -0.0002 ± 0.0003 nmol m^2 s^{-1}. Linalool was mainly deposited to the sorghum plantation (-0.0004 ± 0.0004 nmol m^2 s^{-1}) with a single emission (0.0009 ± 0.01 nmol m^2 s^{-1}) in the last GS3 stage, whereas p-cymene was emitted throughout the whole growing season (0.0007 ± 0.0003 nmol m^2 s^{-1}), with a small uptake during the GS0 stage. Green leaf volatiles (GLVs) exchanges varied in direction and magnitude over the season, with a total average emission of 0.0002 ± 0.0003 nmol m^2 s^{-1} for *cis*-3-hexenol and of 0.00004 ± 0.0003 nmol m^2 s^{-1} for *trans*-2-hexenal. However, both GLVs showed a net emission during the stages GS2 stage (~ 0.002 nmol m^2 s^{-1}), whereas *trans*-2-hexenal were emitted also in the last following GS3 stage (~ 0.003 ± 0.004 nmol m^2 s^{-1}). Toluene and xylenes showed a net average emission during growing season (0.003 ± 0.002 and 0.0004 ± 0.0008 nmol m^2 s^{-1}, respectively) with a higher emission of toluene during the last GS3 stage (0.016 ± 0.005 nmol m^2 s^{-1}). Instead, benzene was mainly deposited during all the growing stages with a total average up take of - 0.0006 ± 0.0006 nmol m^2 s^{-1}. Table 3 reports thestatistics for all detected BVOCs fluxes during the whole sorghum growing season.

VOC	Mean	SE	95th%	5th%	Median	Min	Max	30-min fluxes (N)
Formaldehyde	9.08 10^{-5} (-0.0007)	0.001 (0.001)	0.023 (0.069)	-0.034 (-0.104)	-6.454 10^{-24} (-0.0008)	-0.182 (-0.641)	0.181 (0.409)	647 (3358)
Methanol	-0.004 (0.137)	0.014 (0.013)	0.231 (0.696)	-0.344 (-0.642)	-5.860 10^{-22} (0.048)	-0.774 (-1.747)	2.252 (9.661)	319 (3339)
Acetonitrile	0.002 (0.0005)	0.0009 (0.0006)	0.023 (0.043)	-0.029 (-0.057)	0.002 (0.002)	-0.071 (-0.155)	0.076 (0.177)	378 (3373)
Acetaldehyde	0.007 (0.070)	0.006 (0.004)	0.105 (0.318)	-0.135 (-0.234)	0.0009 (0.026)	-0.424 (-0.836)	1.086 (3.623)	286 (3347)
Formic acid	0.002 (0.013)	0.002 (0.002)	0.041 (0.211)	-0.080 (-0.244)	7.367 10^{-23} (9.99 10-^{5})	-0.350 (-0.920)	0.692 (0.902)	525 (3372)
Acetone/Propanal	-0.002 (0.008)	0.006 (0.002)	0.091 (0.187)	-0.138 (-0.220)	0.004 (0.012)	-1.249 (-1.249)	0.474 (0.766)	272 (3373)
Acetic acid	0.0003 (0.004)	0.0009 (0.001)	0.017 (0.098)	-0.032 (-0.126)	-5.775 10^{-23} (-5.09 10-^{22})	-0.145 (-0.363)	0.192 (0.603)	648 (3363)
m/z 69	0.0009 (0.004)	0.002 (0.001)	0.045 (0.072)	-0.051 (-0.087)	-0.0005 (0.0083)	-0.129 (-0.347)	0.107 (0.280)	301 (3323)
MVK/MAC	-0.0004 (0.0003)	0.0007 (0.0004)	0.014 (0.032)	-0.020 (-0.042)	-0.0003 (-0.0016)	-0.076 (-0.188)	0.051 (0.212)	379 (3373)
Propionic acid	-0.0003 (0.003)	0.0008 (0.002)	0.003 (0.029)	-0.010 (-0.042)	8.733 10^{-26} (1.88 10-^{24})	-0.733 (-1.805)	0.448 (2.299)	1209 (3354)
Benzene	-0.0006 (-0.0006)	0.0008 (0.0006)	0.017 (0.045)	-0.028 (-0.060)	-5.492 10^{-24} (-0.0014)	-0.176 (-0.192)	0.061 (0.272)	442 (3368)
Pentenal	-0.0007 (-0.001)	0.0008 (0.0005)	0.016 (0.033)	-0.020 (-0.050)	-0.001 (-0.0036)	-0.087 (-0.163)	0.065 (0.149)	324 (3373)
m/z 87	0.0006 (0.0008)	0.0005 (0.0003)	0.0125 (0.024)	-0.012 (-0.031)	0.00002 (0.0015)	-0.0466 (-0.122)	0.033 (0.163)	336 (3373)
Toluene	-0.001 (0.002)	0.001 (0.002)	0.015 (0.086)	-0.033 (-0.116)	-1.021 10^{-24} (8.94 10-^{24})	-0.721 (-1.040)	0.213 (1.182)	928 (3369)
trans-2-Hexenal	-0.0007 (0.0001)	0.0005 (0.0003)	0.011 (0.022)	-0.019 (-0.032)	-0.0005 (-0.0006)	-0.078 (-0.122)	0.094 (0.127)	562 (3174)
cis-3-Hexenol	-0.0006 (0.0001)	0.0007 (0.0003)	0.012 (0.025)	-0.019 (-0.034)	-0.0006 (-0.0002)	-0.084 (-0.194)	0.047 (0.116)	270 (3373)
Xylenes	-0.0007 (0.0004)	0.0006 (0.0008)	0.009 (0.060)	-0.019 (-0.080)	-8.359 10^{-23} (-6.45 10-^{23})	-0.245 (-0.285)	0.096 (0.246)	831 (3365)
Octyne/Cyclooctene	-0.0008 (-0.0002)	0.0004 (0.0002)	0.005 (0.015)	-0.010 (-0.024)	-3.285 10^{-5} (0.0004)	-0.178 (-0.178)	0.032 (0.120)	506 (3370)
m/z 113	-2.302 10^{-5} (0.0006)	0.0003 (0.0002)	0.006 (0.019)	-0.011 (-0.025)	4.473 10^{-5} (0.0004)	-0.050 (-0.113)	0.049 (0.105)	520 (3367)
p-Cymene	0.0001 (0.0007)	0.0002 (0.0003)	0.006 (0.021)	-0.009 (-0.028)	2.736 10^{-24} (1.90 10-^{20})	-0.049 (-0.104)	0.052 (0.108)	705 (3335)
Monoterpenes	-6.235 10^{-5} (-0.0002)	0.0005 (0.0003)	0.009 (0.022)	-0.016 (-0.034)	-0.0001 (0.0004)	-0.079 (-0.179)	0.091 (0.121)	489 (3180)
Methyl-chavicol	0.0001 (0.0002)	0.0003 (0.0004)	0.004 (0.012)	-0.006 (-0.019)	-1.267 10^{-24} (-4.55 10-^{24})	-0.079 (-0.227)	0.071 (0.226)	570 (2716)
Linalool/Eucalyptol	8.268 10^{-5} (-0.0004)	0.0003 (0.0004)	0.003 (0.014)	-0.007 (-0.023)	-1.001 10^{-22} (-3.075 10-^{5})	-0.063 (-0.070)	0.034 (0.068)	474 (1682)

Table 3. Summary statistics of BVOCs fluxes (nmol m^{-2} s^{-1}) measured during the period from 1st of June to 23rd of August 2018. Statistical values refer to fluxes that have passed the LoD threshold. In brackets are shown statistical values referred to all the recorded fluxes. SE=standard error; 95th%=95th percentile; 5th%=5th percentile; Min=minimum value; Max=maximum value.

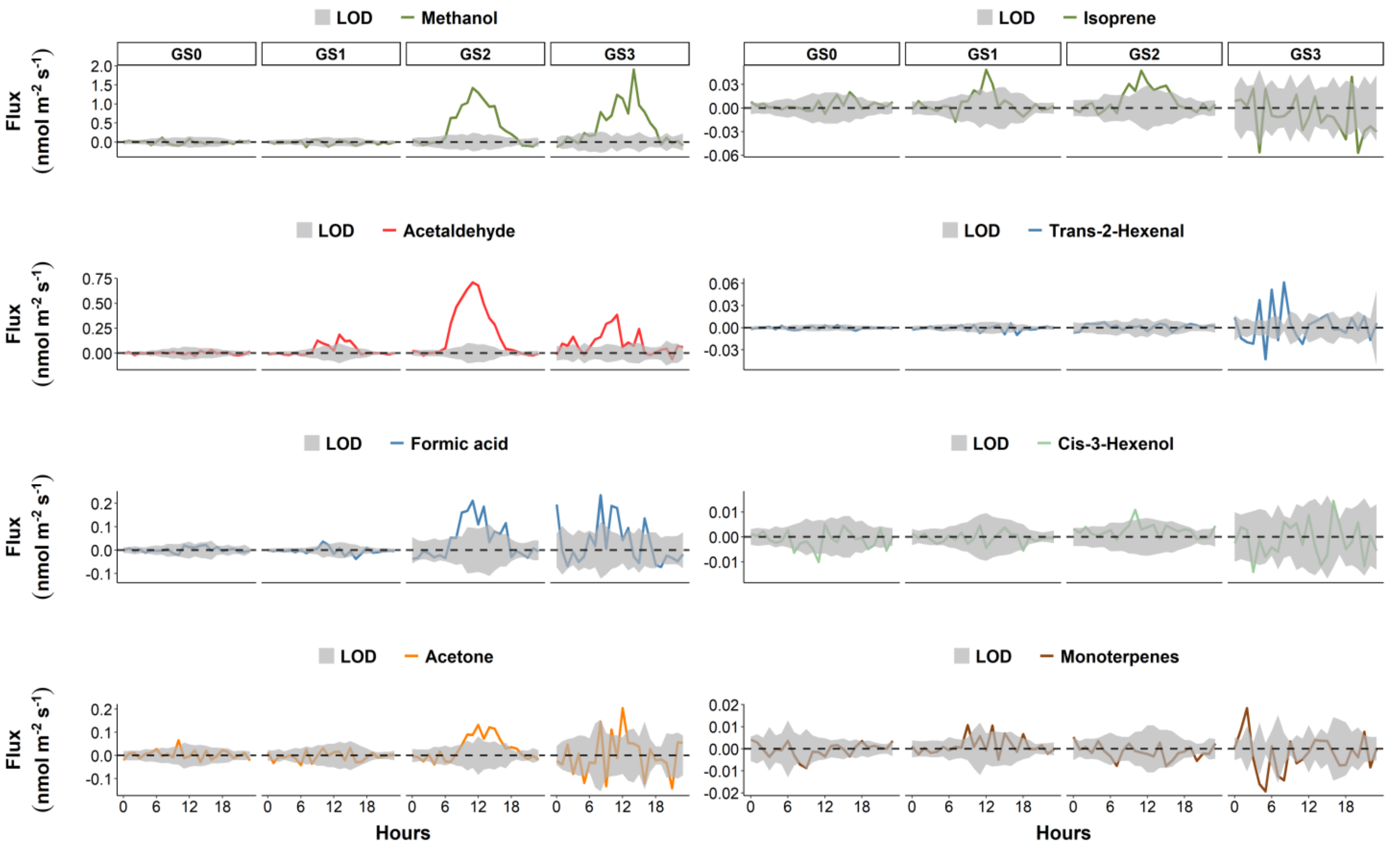

Fig. 3 Daily cycles of half-hourly average fluxes of the relevant BVOCs for each phenological stage. Shaded area represents the limit of detection (LoD) of the fluxes.

BVOCs daily cycles

During the first two phenological stages were not observed clear exchange of BVOCs, with fluxes that did not exceed the LoD (except for the small emission of acetaldehyde among 0.007 and 0.2 nmol m^2 s^{-1} in GS1) and thus were statistically different from zero. Methanol and acetaldehyde show a clear daily pattern during the stage GS2 and GS3, when grain initiation and flowering occur, reaching a maximum of ~ 2 and 0.7 nmol m^2 s^{-1} in the central hours of the day (~14:00 and 11:00, respectively) (Fig. 3; Table 4). Moreover, GS2 and GS3 stages were characterized by lodging and cuttings events (further discussed in the next section). Looking at the weekly daily cycles spanning all the growing season (Fig. 4) it appear clear how emissions of these methanol, acetaldehyde, formic acid and acetone increase with the progression of the growth and flowering. A pronounced emission peak of these four OVOCs characterizes the second-last week (10-16/08) before the end of the observation period, followed by an emission decay in the last week. The *m/z* 69.069, shows a different pattern with a small emission (among 0.005 and 0.03 nmol m^2 s^{-1}) that exceeds the LoD only in the stage GS1 and GS2 (Fig.3), in the full vegetative and reproductive growth, with the emission burst (0.06-0.1 nmol m^{-2} s^{-1}) that occurs in the central hours of the day (Fig.4). Monoterpenes fluxes do not show a clear daily exchange pattern during all the phenological stages, and were always below the LoD (Fig.3) except for small uptake (among -0.03 and -0.005 nmol m^2 s^{-1}) that occur in the first and final part of the observation period during the first hours of the day (Fig. 3; Fig. 4). GLVs (*trans*-2-Hexenal, *cis*-3-Hexenol) resulted almost always below LoD except for the emission peak of *trans*-2-Hexenal (among 0.004 and 0.02 nmol m^2 s^{-1}) in the stage GS3 and *cis*-3-Hexenol (0.01 nmol m^2 s^{-1}) in the stage GS3 (Fig. 3). Looking in details, the GLVs exchange pattern during the weeks (Fig. 4) appears quite scattered around LoD with very small emissions burst (among ~ 0.02 and 0.04 nmol m^2 s^{-1}) in the central and final weeks, when lodging and cuttings events occurs.

Stress-induced BVOCs emission during lodging and cutting events

Throughout the overall sorghum growth period we recognized three lodging events, by pictures collected with the phenological camera. In this study, we report only the fluxes of BVOCs that were related to these stress events and focused our attention only on the second and last lodging event. The first two lodging events did not show significant differences in BVOCs exchanges; instead, the last lodging event occurred after the beginning of the cutting. Details about the date in which occurred lodging and cutting events and statistics are summarized in Table 5. In the results, we always reported time windows with one day before the registered beginning of the event and one day after, to highlight the stress influence on BVOCs emission. During the first lodging event (Fig. 5), methanol fluxes changed continuously between emission and deposition exceeding the LoD, with some emission burst during the day (~1.7 nmol m^{-2} s^{-1}).

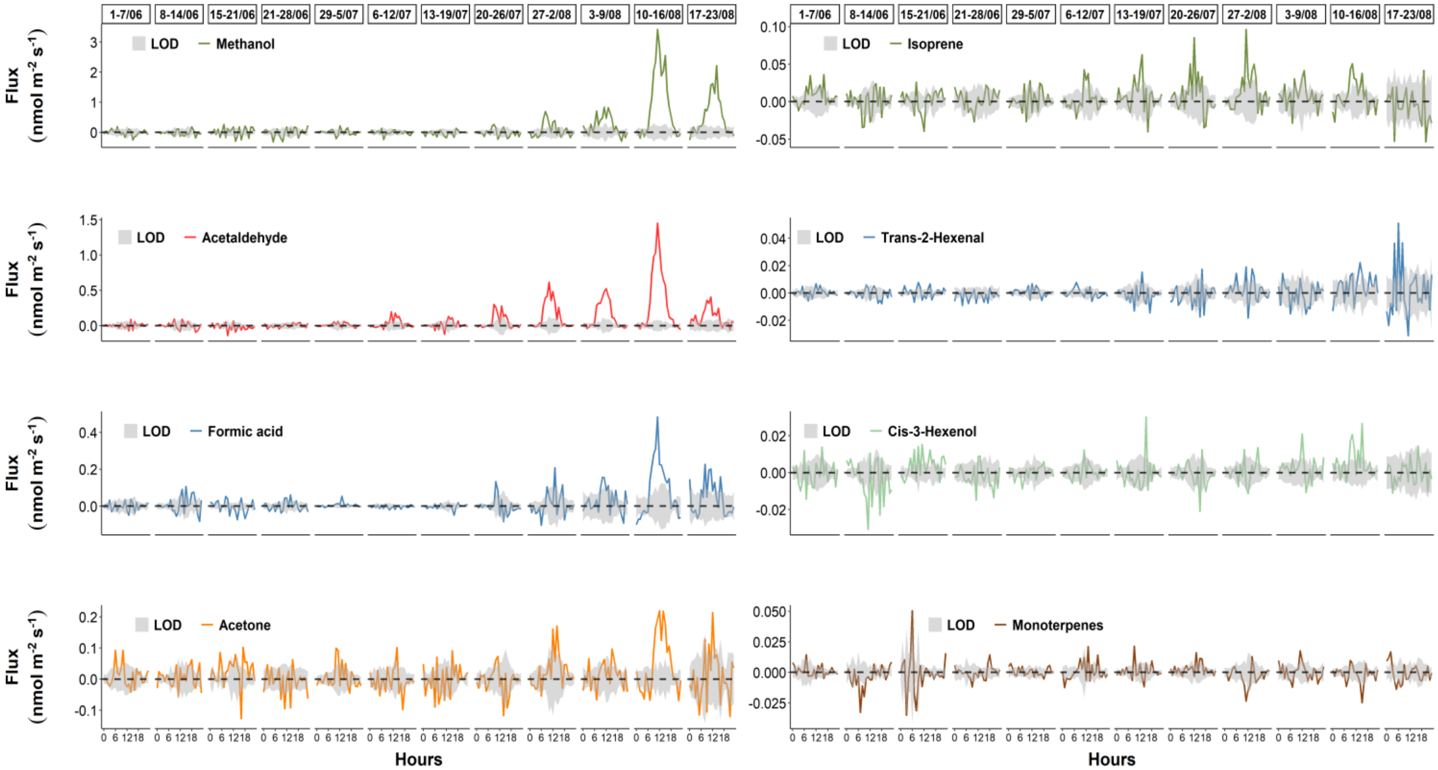

Fig. 4 Daily cycles of half-hourly average fluxes of the relevant BVOCs for each week of the sorghum growing season. Shaded area represents the limit of detection (LoD) of the fluxes.

Acetaldehyde showed a clearer daily cycle with emission peak (~ 1.5 nmol m^{-2} s^{-1}) during the central hours of the day and some uptakes (~ -0.5 nmol m^{-2} s^{-1}). Results showed a similar trend for formic acid and acetone, but with less defined daily cycles (~ 0.5 nmol m^{-2} s^{-1}). The second lodging event (Fig. 6) showed clear daily cycles of methanol with fluxes one order of magnitude higher (~ 10-nmol m^{-2} s^{-1}) than the fluxes recognized in the previous lodging event (Table 5). A similar trend with clear daily cycles was recorded also for acetaldehyde, formic acid and acetone, albeit remaining within the same order of magnitude. During the cutting event (Fig. 7) methanol and acetaldehyde showed clear daily cycles for some days (05-06 for acetaldehyde and 11 August 2018 for methanol and acetaldehyde) into the selected time window, more pronounced for acetaldehyde but within the same order of magnitude than the previous lodging event. Fluxes of formic acid and acetone were very scattered and closed to zero changing direction during the observation period. GLVs have always been emitted during these mechanical stress events, but never showing a clear daily cycle.

Phenological Stage	VOC	Mean	SE	95th%	5th%	Median	Min	Max	30-min fluxes (N)
GS0	Methanol	-0.008 (-0.004)	0.009 (0.010)	0.033 (0.036)	-0.080 (-0.080)	0.0004 (0.0003)	-0.094 (-0.094)	0.092 (0.118)	109 (1169)
	Acetaldehyde	0.0004 (0.0004)	0.003 (0.003)	0.017 (0.016)	-0.020 (-0.020)	-0.0003 (-0.0003)	-0.028 (-0.028)	0.032 (0.033)	109 (1176)
	Formic acid	0.002 (0.002)	0.002 (0.002)	0.018 (0.017)	-0.013 (-0.012)	-0.0007 (-0.0007)	-0.021 (-0.021)	0.022 (0.022)	191 (1196)
	Acetone/Propanal	0.003 (0.004)	0.003 (0.004)	0.022 (0.022)	-0.019 (-0.022)	0.007 (0.002)	-0.028 (-0.028)	0.027 (0.066)	109 (1196)
	m/z 69	0.002 (0.004)	0.001 (0.001)	0.009 (0.011)	(-0.003) (-0.003)	0.001 (0.002)	-0.007 (-0.007)	0.016 (0.020)	102 (1147)
	trans-2-Hexenal	-0.0004 (-0.0003)	0.0003 (0.0004)	0.002 (0.002)	-0.003 (-0.002)	-0.0003 (-0.0002)	-0.002 (-0.003)	0.003 (0.004)	177 (1189)
	cis-3-Hexenol	$3\ 10^{-8}$ (-0.001)	0.0006 (0.0007)	0.003 (0.003)	-0.003 (-0.006)	-0.0004 (-0.001)	-0.004 (-0.009)	0.005 (0.005)	81 (1196)
	Monoterpenes	-0.0004 (-0.0004)	0.0006 (0.0007)	0.003 (0.003)	-0.004 (-0.006)	-0.0001 (-0.00004)	-0.008 (-0.008)	0.004 (0.004)	220 (1194)
GS1	Methanol	-0.003 (-0.015)	0.008 (0.010)	0.058 (0.051)	-0.054 (-0.114)	-0.006 (-0.008)	-0.095 (-0.131)	0.062 (0.062)	118 (960)
	Acetaldehyde	-0.003 (0.030)	0.002 (0.012)	0.005 (0.123)	-0.016 (-0.101)	-0.001 (-0.015)	-0.017 (-0.018)	0.025 (0.186)	76 (961)
	Formic acid	-0.0045 (-0.002)	0.002 (0.0030)	0.008 (0.009)	-0.025 (-0.024)	-0.003 (-0.003)	-0.037 (-0.037)	0.023 (0.037)	241 (966)
	Acetone/Propanal	0.001 (-0.003)	0.003 (0.004)	0.027 (0.023)	-0.027 (-0.034)	-0.001 (-0.002)	-0.028 (-0.042)	0.033 (0.033)	67 (967)
	m/z 69	0.001 (0.005)	0.001 (0.002)	0.008 (0.021)	-0.005 (-0.009)	0.001 (0.0021)	-0.010 (-0.017)	0.009 (0.048)	89 (966)
	trans-2-Hexenal	0.0001 (-0.001)	0.0005 (0.0008)	0.003 (0.003)	-0.002 (-0.008)	-0.0002 (-0.0009)	-0.002 (-0.010)	0.003 (0.006)	155 (961)
	cis-3-Hexenol	-0.0003 (-0.0003)	0.0005 (0.0005)	0.001 (0.001)	-0.004 (-0.004)	-0.0004 (-0.0004)	-0.005 (-0.005)	0.004 (0.004)	71 (967)
	Monoterpenes	0.00002 (0.001)	0.0003 (0.0008)	0.001 (0.006)	-0.002 (-0.002)	-0.00004 (0.0005)	-0.002 (-0.005)	0.002 (0.010)	109 (961)
GS2	Methanol	-0.010 (0.402)	0.020 (0.103)	0.061 (1.084)	-0.085 (-0.091)	-0.007 (0.161)	-0.086 (-0.114)	0.114 (1.418)	65 (933)
	Acetaldehyde	0.0008 (0.198)	0.005 (0.052)	0.019 (0.616)	-0.023 (-0.020)	0.001 (0.039)	-0.024 (-0.024)	0.019 (0.709)	73 (933)
	Formic acid	0.002 (0.041)	0.009 (0.016)	0.058 (0.165)	-0.034 (-0.033)	-0.009 (0.002)	-0.037 (-0.037)	0.080 (0.211)	75 (933)
	Acetone/Propanal	-0.001 (0.029)	0.005 (0.010)	0.027 (0.107)	-0.026 (-0.027)	-0.002 (0.011)	-0.027 (-0.038)	0.045 (0.131)	70 (933)
	m/z 69	0.002 (0.009)	0.002 (0.003)	0.016 (0.030)	-0.007 (-0.006)	0.001 (0.004)	-0.008 (-0.008)	0.022 (0.047)	84 (933)
	trans-2-Hexenal	0.001 (0.001)	0.0008 (0.0008)	0.005 (0.005)	-0.006 (-0.006)	0.002 (0.002)	-0.006 (-0.006)	0.007 (0.007)	201 (872)
	cis-3-Hexenol	0.002 (0.002)	0.0004 (0.0005)	0.005 (0.004)	-0.001 (-0.0008)	0.002 (0.002)	-0.001 (-0.001)	0.004 (0.010)	90 (933)
	Monoterpenes	-0.001 (-0.001)	0.0006 (0.0007)	0.002 (0.002)	-0.005 (-0.007)	-0.001 (-0.001)	-0.007 (-0.008)	0.003 (0.005)	134 (873)

GS3	Methanol	0.037 (0.424)	0.030 (0.106)	0.162 (1.088)	-0.078 (-0.089)	0.027 (0.215)	-0.094 (-0.133)	0.193 (1.903)	27 (277)
	Acetaldehyde	0.022 (0.097)	0.011 (0.023)	0.070 (0.278)	-0.036 (-0.019)	0.034 (0.066)	-0.060) (-0.060)	0.073 (0.385)	28 (277)
	Formic acid	-0.014 (0.029)	0.009 (0.019)	0.039 (0.186)	-0.065 (-0.067)	-0.023 (-0.005)	-0.068 (-0.071)	0.068 (0.234)	18 (277)
	Acetone/Propanal	0.008 (0.00003)	0.013 (0.017)	0.056 (0.095)	-0.051 (-0.130)	-0.001 (-0.012)	-0.120 (-0.141)	0.144 (0.204)	26 (277)
	m/z 69	-0.005 (-0.009)	0.004 (0.005)	0.018 (0.022)	-0.030 (-0.053)	-0.009 (-0.010)	-0.029 (-0.056)	0.025 (0.039)	26 (277)
	trans-2-Hexenal	0.005 (0.003)	0.002 (0.004)	0.015 (0.031)	-0.008 (-0.021)	0.006 (0.001)	-0.010 (-0.042)	0.017 (0.061)	29 (152)
	cis-3-Hexenol	-0.001 (-0.001)	0.001 (0.001)	0.006 (0.006)	-0.011 (-0.011)	-0.002 (-0.002)	-0.011 (-0.014)	0.008 (0.014)	28 (277)
	Monoterpenes	-0.001 (-0.002)	0.001 (0.001)	0.004 (0.006)	-0.009 (-0.015)	$2\ 10^{-6}$ (-0.001)	-0.012 (-0.019)	0.003 (0.018)	26 (152)

Table 4. Summary statistics of selected BVOCs fluxes (nmol m^{-2} s^{-1}) of interest for each phenological stage of the growing sorghum during the period from 1st of June to 23rd of August, 2018. Values refer to fluxes that have passed the LOD threshold. In brackets values refer to all the recorded fluxes. SE=standard error; 95th%=95th percentile; 5th%=5th percentile; Min=minimum value; Max=maximum value.

Discussion

In this section, we discuss BVOCs exchange dynamics investigated over the whole growing season of sorghum cultivated in the Mediterranean area. OVOCs were the most exchanged BVOCs. Methanol emissions predominance was observed through the whole growing season, consistent with many other studies on grasslands and croplands, including maize (Warneke et al., 2002; Das et al., 2003; Custer and Schade, 2007; Bamberger et al., 2010; Eller et al., 2011; Ruuskanen et al., 2011; Copeland et al., 2012; Crespo et al., 2013; Graus et al., 2013; Bachy et al., 2016; Wiß et al., 2017). Acetaldehyde, the second most emitted BVOC from the sorghum field, follows a similar emission pattern than methanol but with a drop into stage GS3 where methanol reach his maximum emission. The different trend of methanol and acetaldehyde during stage GS3 could be explained by the relation of methanol with leaf expansion (described below), which not affect acetaldehyde. Smaller exchange of other OVOCs, along with methanol and acetaldehyde, were observed.

Events	Date	VOC	Mean	SE	$95^{th}\%$	$5^{th}\%$	Median	Min	Max	30-min fluxes (N)
Lodging	23-29/07	Methanol	-0.0004 (0.017)	0.083 (0.026)	0.261 (0.562)	-0.461 (-0.694)	-0.061 (-0.049)	-0.774 (-1.346)	1.655 (1.719)	26 (311)
		Acetaldehyde	0.063 (0.127)	0.038 (0.017)	0.133 (0.518)	-0.062 (-0.183)	0.008 (0.042)	-0.072 (-0.718)	1.086 (1.337)	30 (311)
		Formic acid	0.017 (0.010)	0.022 (0.011)	0.084 (0.267)	-0.075 (-0.290)	0.0004 (-0.014)	-0.351 (-0.622)	0.692 (0.694)	41 (311)
		Acetone/Propanal	0.036 (0.008)	0.027 (0.010)	0.173 (0.219)	-0.117 (-0.271)	0.025 (0.020)	-0.356 (-0.683)	0.474 (0.474)	27 (311)
		trans-2-Hexenal	0.005 (0.001)	0.003 (0.001)	0.014 (0.027)	-0.015 (-0.043)	-0.0001 (0.002)	-0.045 (-0.076)	0.030 (0.080)	68 (304)
		cis-3-Hexenol	-0.003 (0.0002)	0.005 (0.001)	0.023 (0.025)	-0.017 (-0.038)	-0.003 (-0.0001)	-0.101 (-0.071)	0.065 (0.064)	21 (311)
	15-19/08	Methanol	0.106 (1.011)	0.157 (0.113)	0.425 (2.874)	-0.326 (-0.653)	-0.118 (0.595)	-0.431 (-1.610)	2.252 (9.662)	16 (233)
		Acetaldehyde	0.043 (0.242)	0.022 (0.023)	0.106 (0.722)	-0.047 (-0.137)	0.036 (0.128)	-0.082 (-0.373)	0.322 (2.145)	17 (233)
		Formic acid	0.044 (0.140)	0.039 (0.016)	0.161 (0.392)	-0.115 (-0.227)	0.069 (0.179)	-0.130 (-0.542)	0.188 (0.650)	9 (233)
		Acetone/Propanal	0.009 (0.038)	0.020 (0.011)	0.069 (0.235)	-0.071 (-0.225)	0.007 (0.067)	-0.088 (-0.676)	0.135 (0.525)	10 (233)
		trans-2-Hexenal	0.0004 (0.004)	0.002 (0.003)	0.018 (0.060)	-0.016 (0.055)	-0.003 (0.004)	-0.020 (-0.121)	0.028 (0.128)	37 (197)
		cis-3-Hexenol	0.001 (0.004)	0.001 (0.002)	0.007 (0.0026)	-0.006 (-0.031)	-0.001 (0.007)	-0.008 (-0.194)	0.018 (0.092)	26 (233)
Cutting	05-10/08	Methanol	0.082 (0.341)	0.080 (0.041)	0.510 (1.068)	-0.345 (-0.075)	0.054 (0.366)	-0.357 (-1.329)	0.580 (3.364)	16 (320)
		Acetaldehyde	-0.001 (0.188)	0.015 (0.023)	0.057 (0.655)	-0.083 (-0.153)	0.002 (0.082)	-0.146 (-0.396)	0.168 (2.140)	20 (320)
		Formic acid	0.023 (0.022)	0.030 (0.014)	0.181 (0.320)	-0.198 (-0.328)	0.020 (0.029)	-0.228 (-0.500)	0.344 (0.692)	24 (320)
		Acetone/Propanal	-0.019 (0.019)	0.014 (0.009)	0.051 (0.225)	-0.113 (-0.216)	-0.027 (-0.014)	-0.138 (-0.412)	0.219 (0.620)	26 (320)
		trans-2-Hexenal	0.0005 (-0.001)	0.003 (0.002)	0.016 (0.032)	-0.021 (-0.035)	0.005 (-0.003)	-0.074 (-0.074)	0.094 (0.094)	52 (272)
		cis-3-Hexenol	0.004 (0.004)	0.002 (0.001)	0.012 (0.030)	-0.009 (-0.031)	-0.002 (0.006)	-0.016 (-0.075)	0.034 (0.106)	29 (320)

Table 5. Summary statistics of selected BVOCs fluxes (nmol m^{-2} s^{-1}) for two lodging events and a cutting event occurred during the period from 1st of June to 23rd of August, 2018. Values refers to fluxes that have passed the LOD threshold. In brackets are values referred to all the recorded fluxes. SE=standard error; $95^{th}\%$=95th percentile; $5^{th}\%$=5th percentile; Min=minimum value; Max=maximum value.

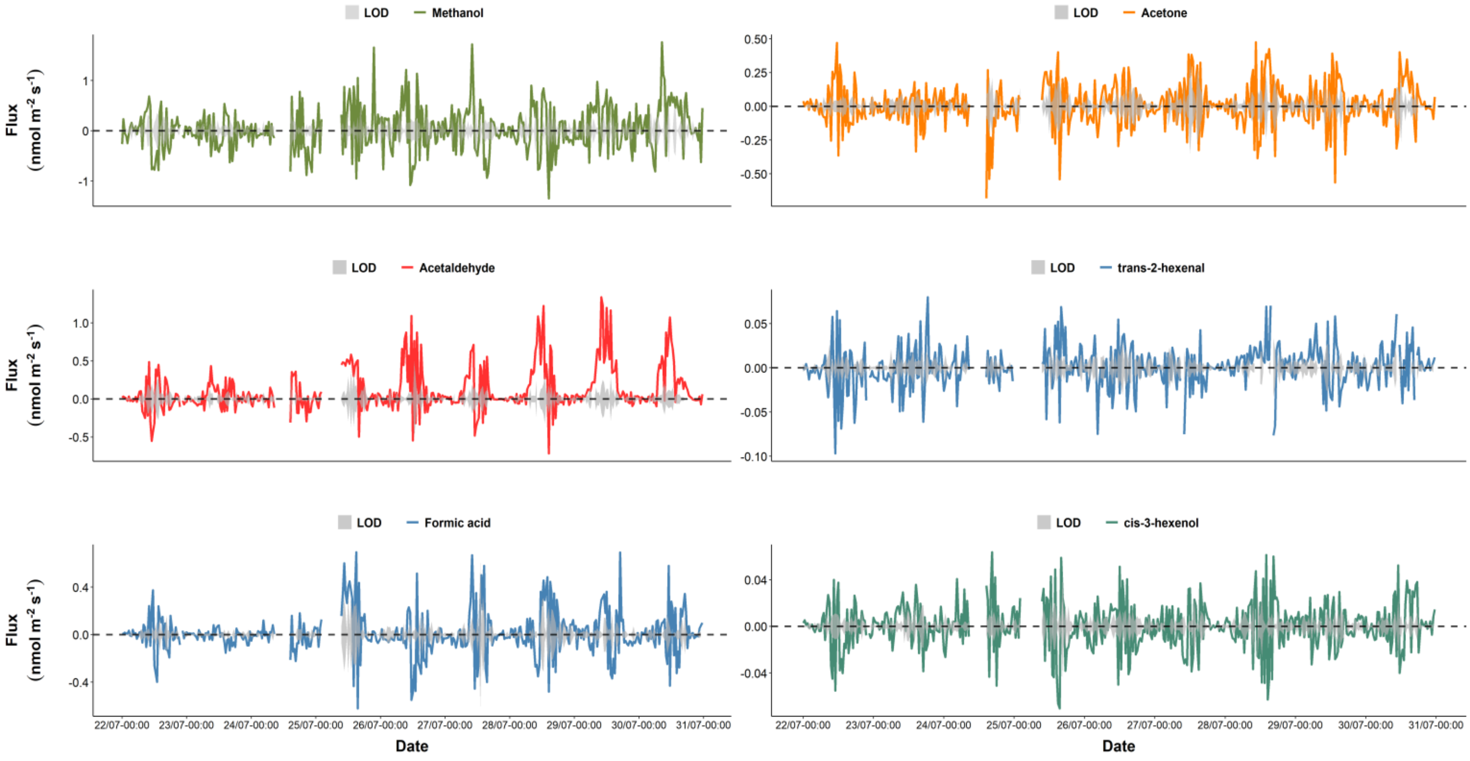

Fig. 5 Half-hourly average fluxes of the relevant BVOCs during the first lodging events. Shaded area represents the limit of detection (LoD) of the fluxes. See Table 5 for details.

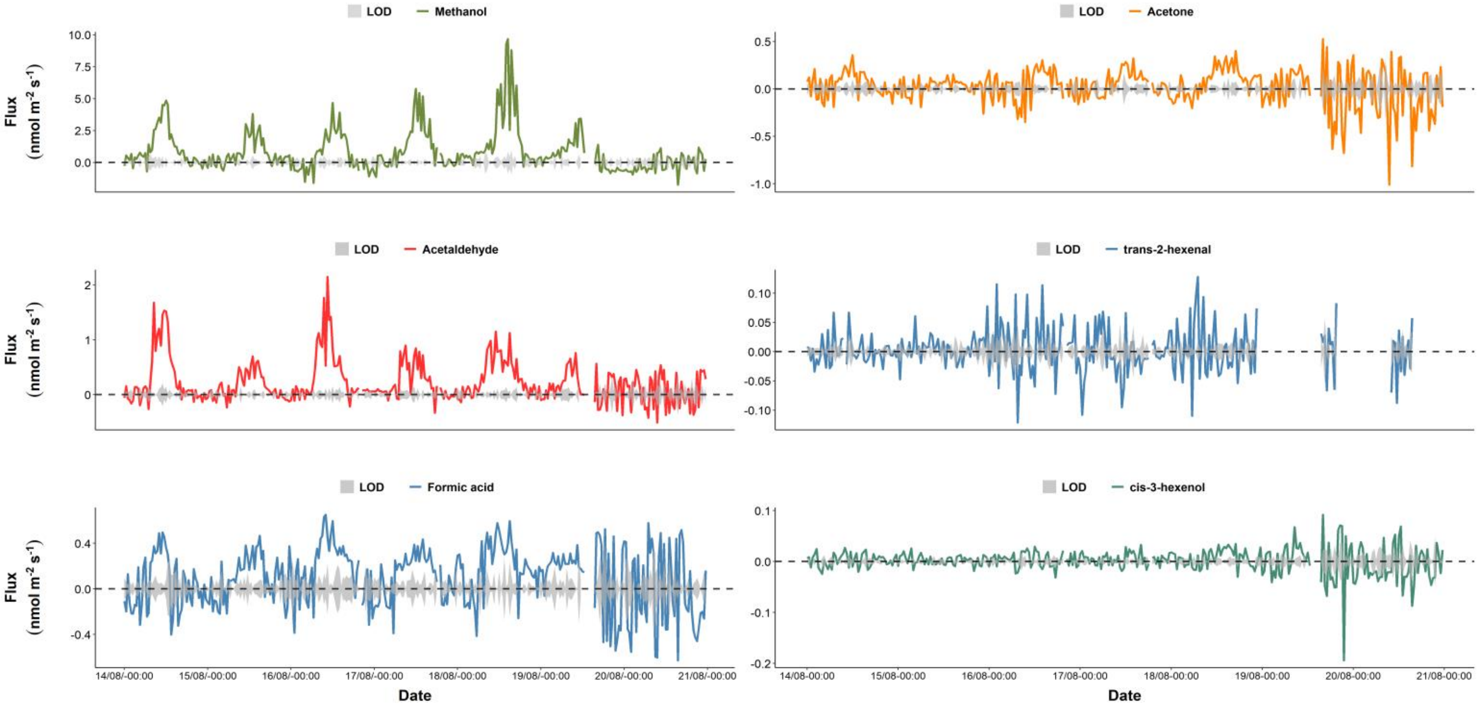

Fig. 6 Half-hourly average fluxes of the relevant BVOCs during the second lodging events. Shaded area represents the limit of detection (LoD) of the fluxes. See Table 5 for details.

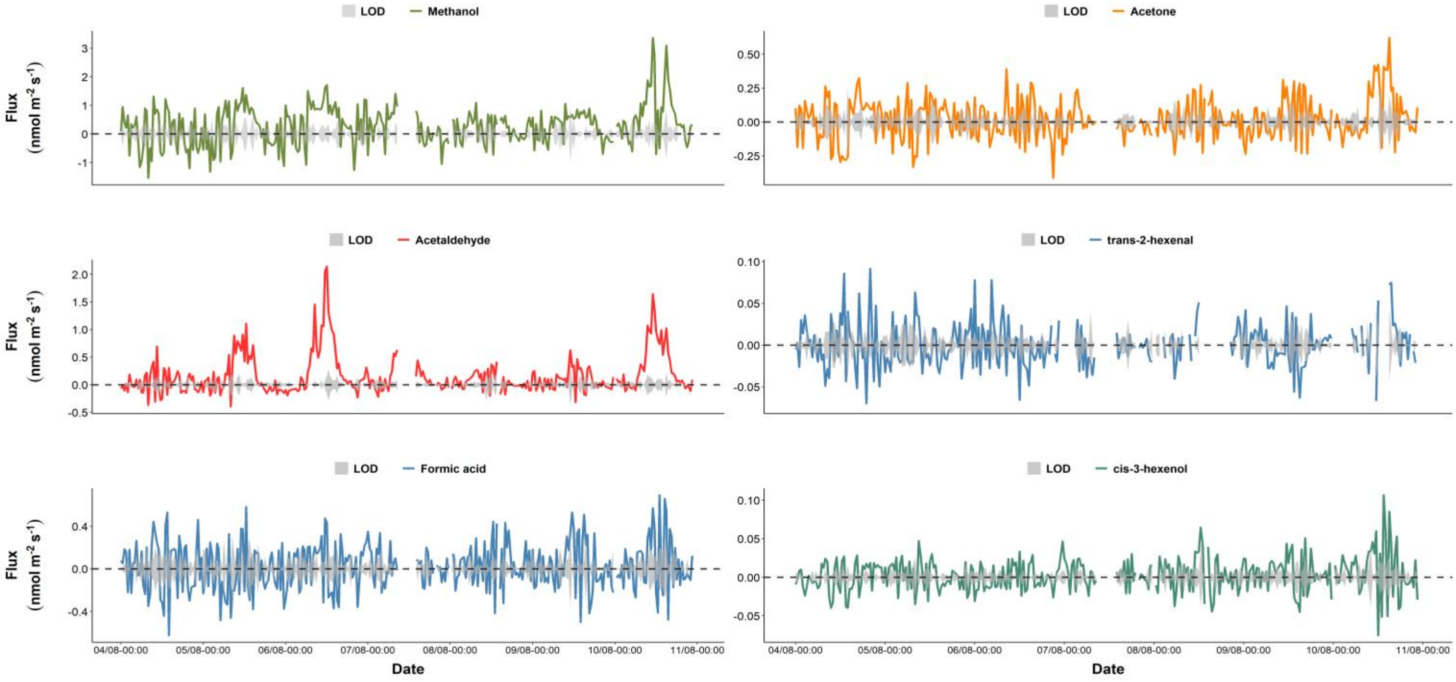

Fig. 7 Half-hourly average fluxes of the relevant BVOCs during the cutting event. Shaded area represents the limit of detection (LoD) of the fluxes. See Table 5 for details.

Smaller emissions and deposition of other OVOCs, along with methanol and acetaldehyde, were observed. In particular, formic acid and acetone seem to follow the same dependency to the phenology of the two other most emitted BVOCs. Methanol, acetaldehyde and acetone emissions were observed from maize leaves (Graus et al., 2013), from sorghum in laboratory experiments simulating leaf-drying/senescence (Karl et al., 2005) and from maize, wheat and rapeseed in dynamic chambers (Gonzaga Gomez et al., 2019). As far as we know, formic acid exchanges have never been reported before for crop plant species or in agricultural ecosystems. Thus, at ecosystem-scale, our results show that OVOCs exchange from sorghum increased as soon as plants developed and biomass increased. Higher OVOCs emissions occured during stage GS2 when GAI reached his maximum, according to the hypothesis that OVOCs emissions are related to leaf growth (Graus et al., 2013, Mozaffar et al., 2017). Indeed, during cell wall expansion methanol is produced by demethylation of pectins catalyzed by Pectin Methyl Esterase (PME) activity (Nemecek-Marshall et al., 1995; Fall and Benson, 1996) and methanol emissions have been shown to correlate with plant growth rates (Hüve et al., 2007). Moreover, temperature affects both methanol production rate (Nemecek-Marshall et al., 1995) than partitioning among the aqueous and gaseous pools within the leaves (Niinemets and Reichstein, 2003). In addition, light intensity modulates stomatal aperture and then actively regulates methanol diffusion from the site of production to the atmosphere (Niinemets et al., 2004). In particular, formic acid can originate from methanol metabolization in plants and, because its toxicity, be released out of the leaves (Cossins, 1964). However, formic acid along with acetic acid can also be formed in the atmosphere from formaldehyde and acetaldehyde oxidation processes (Bode et al., 1997; Kesselmeier et al., 1997). The physiological mechanisms of acetaldehyde production in plants is not completely understood yet, but seems to be mostly related to stressful conditions (Seco et al., 2007). Moreover, in contrast with the findings of Bachy et al (2016), in our study soil does not seem to play an important role in the BVOCs exchange. In fact, while we did not record significant detectable fluxes of BVOC from the bare soil (at GS0), Bachy et al (2016) reported strong uptake of both acetic acid and methanol, as well as emissions of acetone and acetaldehyde of the same order of magnitude as from maize in the full-developed stage. In our study, only acetone and formic acid show small emissions (~ 0.1 nmol m^{-2} s^{-1}) from bare soil (Fig. 2; Fig 3; Fig 4). Bachy et al. (2016) found that soil was the largest source of acetone; however, acetone emissions could also originate from photochemical reactions of other BVOCs (as methylbutenol and terpenes) occurring in the atmosphere. Our results showed emissions of a protonated ions related to *m/z* 69 (i.e. isoprene) in the central phenological stages of sorghum growth, with daily diurnal variation following temperature and PAR (Fig.1; Fig 3; Fig 4). We are not able to indentify *m/z* 69 as isoprene, but we know that isoprene emissions were found for maize, wheat and rapeseed at leaf level (Evans et al., 1982; Gonzaga Gomez et al., 2019) and Bachy et al. (2016) reported isoprene emission during the whole maize growing season at the ecosystem level. Differently from the observations reported for maize (Das et al., 2003; Wiß et al., 2017), sorghum was not an important monoterpenes source but rather a small sink (Fig. 2; Fig. 4), consistent with the results of Bachy et al. (2016) for maize field. Significant amounts of reactive monoterpenes play an important role in regional secondary organic aerosol (SOA) formation (Joutsensaari et al., 2005) and are considered in regional biosphere-atmosphere feedback analysis, looking at land-use change scenarios that evaluate the impacts of cropland production. However, for what concern sorghum growing in the Mediterranean area, we can assert that the release of monoterpenes that may impact on SOA formation can be negligible. Sorghum was a clear benzene sink, as reported also by Bachy et al. (2016) for the maize, whereas toluene and xylenes showed emissions during the whole sorgum growing season. This would be partially in agreement with the findings of Graus et al. (2013) on maize that found emission of benzene and toluene from leaves. In fact, in our case only toluene was emitted, according to White et al. (2009) but in contrast with Bachy et al. (2016) on maize. GLVs exchanges were very low with both emission and deposition fluxes. Small diurnal emissions bursts (~ 0.02-0.04 nmol m^2 s^{-1}) occurred in some weeks in the middle and at the end (from 06 July to 23 August 2018) of the observations period (Fig. 4), when mechanical stress of lodging and cutting occurred. Nevertheless, methanol, acetaldehyde, formic acid and acetone were largely emitted. Methanol, acetaldehyde, acetone and GLVs emissions from cutting have been already observed in several studies (Karl et al., 2001; Warneke et al., 2002; Oloffson et al., 2003; Davison et al., 2008; Bamberger et al., 2010, Ruuskanen et al., 2011, Brilli et al., 2012). To our knowledge, no BVOCs exchanges have been reported before in relation to lodging events at ecosystem scale. After lodging and cutting (Fig 5; Fig 6; Fig 7; Tab 5), the most responsive fluxes of BVOCs followed a pronounced diurnal cycle (with emissions peaking during daytime before to decrease to zero during nighttime) showing an amplitude that steadily decreased over time, according to what observed by Brilli et al. (2012). Acetaldehyde flux emissions showed a clear diurnal cycle after lodging events. In particular, the second lodging event showed a more pronounced daily emissions than the firs one, probably because it occurred after cutting which emissions influenced the subsequent lodging. In fact, cutting also showed acetaldehyde and methanol emission along with smaller fluxes of acetone and formic acid. Unfortunately, the overlapping of the two events of cutting and lodging make difficult a proper characterization of the second lodging event. In addition, although methanol was the most emitted flux of BVOC during these events (Table 5), acetaldehyde always showed a much clear daily cycle. Besides growth, it is known that pectin methyl esterase (PME) is involved in processes that impact on cell wall structure inducing methanol emissions, like leaf abscission, biotic and abiotic injuries and senescence (Bachy et al., 2016; Karl et al., 2005; Mozaffar et al., 2018). This process would explain why in our study high methanol emissions occurred in the last part of the growing season as well as in response to mechanical stress. Acetone emissions from plants also have been correlated with different stress conditions, such as mechanical wounding, ozone exposure, and flooding episodes (Seco et al., 2007). Emissions of formic acid has never been reported before in relationship with either cutting or mechanical stress events, but it may have been originated from the metabolization of the high methanol content within leaves in the final development stages (Cossins, 1964). As reviewed by Seco et al. (2007), acetaldehyde emissions have been related to different types of stress (mechanical, herbivory, ozone exposure and anoxia condition). Acetaldehyde may also originate as result of 'pyruvate overflow mechanism' when pyruvate is accumulated into cytosol during light–dark transitions (Karl et al., 2002). Moreover, Graus et al. (2004) proposed a third pathway, which involve acetyl-CoA conversion to acetaldehyde during light-dark transitions and wounding. In the experimental condition of this study, light-dark transitions are unlikely to contribute significantly to acetaldehyde emissions under field conditions. During lodging events, a portion of tall sorghum plants covers other plant individuals, reducing the incoming PAR and thus simulating a light-dark transition in the lower layers of the crop canopy. Moreover, lodging events most likely cause anoxic conditions, because plants in the top layer create a close tight canopy that reduce the oxygen availability for the underlying plants and soil. However, without any more specific detail on the acetaldehyde production in sorghum occurred during lodging, we can only conclude that probably all three kind of stress (anoxic condition, light-dark transition and mechanical wounding) can be responsible for the constant and high acetaldehyde emission fluxes we have recorded in our study. As GLVs emissions are always reported in relation to cutting and mechanical stress (Karl et al., 2001; Warneke et al., 2002; Oloffson et al., 2003; Davison et al., 2008; Bamberger et al., 2010; Ruuskanen et al., 2011; Brilli et al.; 2012), we recognized GLVs emission in our measurements but whitout a clear daily cycle. This is probably due to the chemical instability of GLVs and/or to the transient nature of their formation after wounding (Fall et al., 1999; Brilli et al. 2011). Finally, we are aware that there are not many studies with direct flux measurements on crops at ecosystem scale and that could be useful provide emission in the form of Basal Emission Factor for global emission models. However, because this work is in preparation, this calculation is still work in progress.

Conclusions

This study report BVOCs exchanges over a sorghum field during a whole growing season in the Mediterranean area. OVOCs represent the main exchanged BVOCs from sorghum, dominated by methanol and acetaldehyde emissions. Bi-directional exchanges of formic acid, acetone, formaldehyde and MVK/MAC were also recorded, along with acetic acid emissions. In particular, formic acid exchange has never been reported before for crop species and agricultural ecosystems. Fluxes of OVOCs appear to follow sorghum growth rate throughout the phenological stages, in relation to the physiological pathway of leaf expansion and mechanical stresses response. Emission fluxes of protonated ions (m/z 69.096) which may be related to isoprene were also detected in the central development stage, following diurnal pattern lead by PAR and temperature. Monoterpenes were poorly exchanged and mainly taken-up by the sorghum ecosystem, with a negligible impact on SOAs formation in this area. Deposition of benzene was observed during the whole growing season, whereas toluene and xylenes were mainly emitted. GLVs were poorly emitted, throughout the growing season, except for some small diurnal emission bursts concurring with lodging and cutting stress events. During the first phenological phase when the sorghum ecosystem was mainly characterized by bare soil, no relevant flux of BVOCs was found except for a small acetone and formic acid emissions. Although BVOCs exchange during mechanism stress due to cutting is well documented, for the first time in this study we report BVOCs fluxes related to plants lodging. .This study shows a lodging and a cutting event followed by another lodging event. The second lodging event showed clearer and higher diurnal emissions of stress-related BVOCs than the first lodging, probably because the overlapping with the cutting events increased the air mixing ratio over the sorghum canopy in that period. Methanol, acetaldehyde, acetone and formic acid were the main emitted compounds in relation to these mechanical stress events. Specifically, methanol most likely was emitted because its high concentration in the cellular interspace due to the PME activity. Formic acid, never reported before in relation to cutting and lodging, could likely originate from methanol metabolization. Acetaldehyde emissions during lodging may have several reasons, but it is not possible to discern them without more detailed physiological and biochemical analysis. Probably acetaldehyde during lodging can originate from the contemporary occur of anoxic stress, light-dark transition and mechanical wounding. Finally, GLVs emission pattern were recognized during these mechanical stresses but whitout celar daily cycles, probably because of their instable chemical nature and transient formation after a mechanical damage.

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4. Overall conclusion

During this PhD program, the exchange of VOC has been investigated between the atmosphere and two different type of ecosystems both located in the Mediterranean area. Moreover, different methodologies to perform this investigation at several scales, making use of the most recently developed and reliable technologies available nowadays, were employed. Two ecosystems characterizing Mediterranean area in Southern Italy were chosen: an anthropic ecosystem and an agricultural ecosystem. As for the anthropic ecosystem, an illegal landfills which characterized history and chronicles of the last three decades in Southern Italy, specifically in Campania region was considered. Not only carbon dioxide and methane emissions compose landfills biogas, but also reactive and likely toxic VOCs were detected. These VOCs emissions can sum and interact with the constitutive emissions of BVOCs by plants, which largely exceed the anthropogenic emissions. In particular agricultural areas cover the 35% of the Earth world surface nowadays, in order to satisfy the world human growing population food and energy demand, further contributing to BVOCs budget. Crop plants are widely spread in the Mediterranean area, with many different species and management practices. BVOCs can be reactive and anthropogenic VOCs can be toxic for human health, and thus both are key players in the pollution formation once released in the atmosphere. Due to the high particulate and ozone concentrations as well as environmental conditions that promote photochemical processes, Mediterranean area is a "hot spot" of climate change. In this scenario is necessary to investigated all the potential sources of VOCs.

In the first field study, VOCs composition and emission from an illegally managed waste landfills were investigated, performing monthly punctual measurements directly from collection pipes or soil fractures in seven landfills and a multitude of VOCs was detected and quantified. This study showed that toxic compounds were certainly present in the gaseous emission of the landfills, and some of them seemed to be associated with past dumping of toxic waste. High arenes, MEK and chlorinate compounds emissions appeared as clear sign of plastic, solvents and industrial refuse into the waste. On the other hand, the limited contribution of D-limonene and the higher concentrations of p-Cymene among the terpenes indicated a prolonged waste degradation and biochemical waste aging. Moreover, yearlong atmospheric dispersion modeling showed that the potential impact of toxic VOC on human health estimated by their emission rates were not sufficient "*per se*" to induce acute or chronic diseases in the local population. VOCs landfill emissions could however contribute to ozone and particle formation when mixed with all the other VOCs, NOx and particle sources typical of the Mediterranean area and particularly present within the Naples-Caserta territory.

The second field study was carried out on the same anthropogenic ecosystem, employing for the first time a PTR-TOF-MS to estimate the concentration of all the VOCs detected in the air surrounding the illegally managed waste landfill. Real-time concentration fluctuations of important VOCs belonging to several classes (oxygenated compounds, arenes, terpenes, sulfur compounds) were characterized. The results showed that the lower mass range group gives the major contribution to the total VOCs burden in summer, whereas this trend change in autumn, probably due the higher production of the short-chain OVOCs during summer. Real-time concentration fluctuations show how OVOC are the most abundant VOCs in summer, with a clear daily cycle driven by temperature. Methanol dominated OVOCs emission, originating from microbial alcohol formation in waste degradation. Other OVOC, like acetic and formic acid, appear more abundant in autumn, probably due secondary production and photochemical conversion during summer. According to the previous work, arenes show concentrations dominated by toluene and a pronounced daily trend. MEK daily concentrations in both seasons confirm the xenobiotic sign of these landfills because of the illegally dumping of plastic, solvents and industrial waste, along with arenes. Notwithstanding, benzene always showed concentrations below the EEA limit of 5 $\mu g/m^{-3}$. Odor-causing terpenes and sulfur compounds deriving from fermentation of vegetable and organic matter, showed higher concentrations in autumn because they undergo a certain degree of photo-oxidation in summer.

Lastly, acetonitrile was found, albeit in low concentrations, and never reported before in the biogas of illegal landfills. These results, albeit by agreeing with the previous work in the same landfill area, bring some new information. In fact, the two methodologies employed, TD-GC-MS and PTR-TOF-MS, allowed: (i) the detection and quantification of oxygenated and sulfur compounds always difficult to collect in adsorbent tube; (ii) the estimation of daily concentration fluctuations on a long period of time spanning two different season; (iii) the understanding of the advantages and disadvantages of the two methodologies studying VOCs exchange in a landfill site, employing for the first time PTR-TOF-MS for real-time estimation of VOCs concentration from the landfill biogas. It is to underline that TD-GC-MS and PTR-TOF-MS investigated landfill VOCs exchange and composition from two different spatial and temporal scales.

Lastly, we employed PTR-TOF-MS t BVOCs exchanges over a sorghum field during a whole growing season in the Mediterranean area. This research contributed to improve knowledge about BVOCs exchange from agro-ecosystems. Furthermore, the few reports available never investigated sorghum and croplands in the Mediterranean area. OVOCs were the main exchanged compounds from sorghum dominate by methanol and acetaldehyde. Bi-directional exchanges of formic acid, acetone, formaldehyde and MVK/MAC were also recorded, along with acetic acid emissions. For the first time, in this study, formic acid exchanges from crop species and agro-ecosystem were reported. OVOCs exchanges followed growth rate and phenology, in relation to physiological pathway of leaf expansion and mechanical stresses response. Small diurnal emission pattern of *m/z* 69 were detected, following PAR and temperature in the central phenological stages. Instead, monoterpenes showed poor emission and up-take from the ecosystem, thus not representing a significant contribution toSOAs formation in the Mediterranean climate. Depositions of benzene, toluene and xylenes emission were also observed. GLVs showed small diurnal emission burst concurrently with lodging and cutting stress events, but without show a clear diurnal cycle. No relevant BVOCs exchanges occurred over bare soil during the first phenological phase, differently from other studies on crops. BVOCs exchanges during cutting and lodging events were also observed in this work. Although BVOCs exchange during cutting is well documented, for the first time in this study we report BVOCs fluxes related to lodging as mechanical stress. Between the two lodging events, the second one showed clearer and higher diurnal emissions of stress-related BVOCs, probably because the overlapping with the previous cutting events, increased the air mixing ratio over the field in that period. Methanol, acetaldehyde, acetone and formic acid were the main emitted compounds in relation to these mechanical stress events. Several physiological and biochemical pathways regulate these stress-related emission, varying from compounds to compound. Acetaldehyde emissions during lodging, never reported before, may have several reasons, but it is not possible to discern them without biochemical analysis. Probably acetaldehyde during lodging can originate from the contemporary occur of anoxic stress, light-dark transition and mechanical wounding.

In conclusion, reactive oxygenated compounds dominate VOCs exchanges in the Mediterranean area, albeit derive from different sources. Both anthropic landfill ecosystem and agricultural ecosystem produce substantial OVOCs quantities, involving several different processes: organic matter degradation, waste decomposition, leaves physiological processes during crop development and secondary atmospheric production. This information is added to the already consistent inventory of VOCs emission sources in the Mediterranean area, making necessary further studies to better understand the atmospheric dynamics of reactive OVOCs in this climatically sensitive area. Findings about biogas VOCs composition and concentrations, suggest that VOCs may be use as markers of waste composition, landfill aging state and waste degradation degree. Finally, results from the study on *Sorghum bicolor L.* BVOCs emissions show that these trace gases can act as markers of crop development state, stress state and yield reduction, although the processes that drive these emissions are not entirely clear and need further investigation. These results have scientific and practical importance. They come to fill the lack of information about VOCs exchanges by landfills and crops. Furthermore, they may give practical information to farmers and agricultural companies about crop managing and yielding optimization and contemporary to institutional and governmental organization for waste and landfill managing.