



Surface emission determination of volatile organic compounds (VOC) from a closed industrial waste landfill using a self-designed static flux chamber



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HIGHLIGHTS

- A flux chamber was used to measure VOC surface emissions in a closed landfill.
- The emission rates of 60 different VOC were calculated.
- Aldehydes, acetic acid and ketones were the main emitted VOC.
- Total VOC emissions ranged from 77 ± 17 to 237 ± 48 g day⁻¹, depending on the method used.
- Highest total VOC emissions were observed in the lastly filled landfill bucket.

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ABSTRACT

Closed landfills can be a source of VOC and odorous nuisances to their atmospheric surroundings. A self-designed cylindrical air flux chamber was used to measure VOC surface emissions in a closed industrial landfill located in Cerdanyola del Vallès, Catalonia, Spain. The two main objectives of the study were the evaluation of the performance of the chamber setup in typical measurement conditions and the determination of the emission rates of 60 different VOC from that industrial landfill, generating a valuable database that can be useful in future studies related to industrial landfill management. Triplicate samples were taken in five selected sampling points. VOC were sampled dynamically using multi-sorbent bed tubes (Carbotrap, Carboxen 569) connected to SKC AirCheck 2000 pumps. The analysis was performed by automatic thermal desorption coupled with a capillary gas chromatograph/mass spectrometry detector. The emission rates of sixty VOC were calculated for each sampling point in an effort to characterize surface emissions. To calculate average, minimum and maximum emission values for each VOC, the results were analyzed by three different methods: *Global*, *Kriging* and *Tributary area*. *Global* and *Tributary area* methodologies presented similar values, with total VOC emissions of 237 ± 48 and 222 ± 46 g day⁻¹, respectively; however, *Kriging* values were lower, 77 ± 17 g day⁻¹. The main contributors to the total emission rate were aldehydes (nonanal and decanal), acetic acid, ketones (acetone), aromatic hydrocarbons and alcohols. Most aromatic hydrocarbon (except benzene, naphthalene and methyl-naphthalenes) and aldehyde emission rates exhibited strong correlations with the rest of VOC of their family, indicating a possible common source of these compounds. B:T ratio obtained from the emission rates of the studied landfill suggested that the factors that regulate aromatic hydrocarbon distributions in the landfill emissions are different from the ones from urban areas. Environmental conditions (atmospheric pressure, temperature and relative humidity) did not alter the pollutant emission fluxes.

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1. Introduction

Volatile organic compounds (VOC) can migrate from waste materials buried in landfills and eventually be diffused into the atmosphere, making landfills a source of VOC and odorous nuisances (Lee and Jones-Lee, 1994; Kim and Kim, 2002; Zou et al., 2003; Scheutz et al., 2008; Chemel et al., 2012). Additionally, VOC can act as irritants to the human organism and can have negative health effects (Bernstein et al., 2008; Milner et al., 2011; Carazo Fernández et al., 2013). In municipal solid

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Table 1

Type of waste and quantities deposited at the studied landfill.

Source: CTM (2003) and IDOM (2008a).

Zone	Year	Waste buried	Waste type	Volume (m ³)	Superficial extension (ha)	Maximum waste depth (m)	Site original substrate	Porosity (%)
North-East bucket	1982–1988	Construction and demolition	Inert	590,000	5.22	25	Silt and clay	39
North bucket	1982–1988	Industrial	Nonspecial	210,000	1.63	18	Clay	24.5
		Clay and silt soils	Inert					
South bucket	1988–1995	Miscellaneous	Inert	1,650,000	10.44	38	Silt	33
		Industrial	Nonspecial					
		Aluminum scrap melting salts	Special					

waste landfills, VOC generally represent a small percentage in the total landfill gas, less than 1% (Scheutz et al., 2003; Tassi et al., 2009). VOC final emissions to the atmosphere will be influenced by their formation depending on the type of waste buried, its decomposition processes and the stage reached in these processes (Zou et al., 2003; Chiriac et al., 2011); and their degradation by: microorganisms in the landfill cover soil and the presence of a biocover (Scheutz et al., 2003, 2008; Barlaz et al., 2004; Tassi et al., 2009). In industrial waste landfills, however, VOC percentage in landfill gas and their emissions to the atmospheric environment can be higher due to the nature of the deposited waste.

Flux chambers are direct measurement methods and have been widely used for the assessment of pollutants' emissions to the atmosphere from area sources (Hudson and Ayoko, 2008; D. Parker et al., 2013; D.B. Parker et al., 2013; El-Fadel et al., 2012). Two main types of cylindrical flux chambers are extensively used: static and dynamic flux chambers, both having assets and drawbacks, and generally presenting substantial differences in measured fluxes depending on the chamber design, operation and flux calculation methods (Gao and Yates, 1998;

Lindberg et al., 2002; Hudson and Ayoko, 2008; Liu and Si, 2009; Pedersen et al., 2010; Christiansen et al., 2011; D. Parker et al., 2013; Pihlatie et al., 2013). Dynamic flux chambers commonly supply high flows of clean sweep air or inert gas into the chamber ($2\text{--}30\text{ l min}^{-1}$) (Hudson and Ayoko, 2008), leading to calculated emission rates highly depending on the flushing air flow rates applied (Lindberg et al., 2002). On the other hand, static flux chambers may be influenced by increase in pressure due to chamber installation, leading to underestimation of pollutant's emission rates (Hudson and Ayoko, 2008).

In this manuscript we propose a flux chamber design to evaluate VOC emissions from surfaces through VOC sampling with active multi-sorbent tubes and a further analysis with a TD-GC/MS system, which allows a good chromatographic separation and sensitivity, and low limits of detection indispensable for the quantification of the target compounds. The presented configuration supplies a very low flow rate of clean inert gas (helium) into the flux chamber (100 ml min^{-1}), the same flow that is extracted through the sampling ports. With this design we try to avoid the overestimation of the emission rates due to the

**Fig. 1.** General landfill location and sampling points.

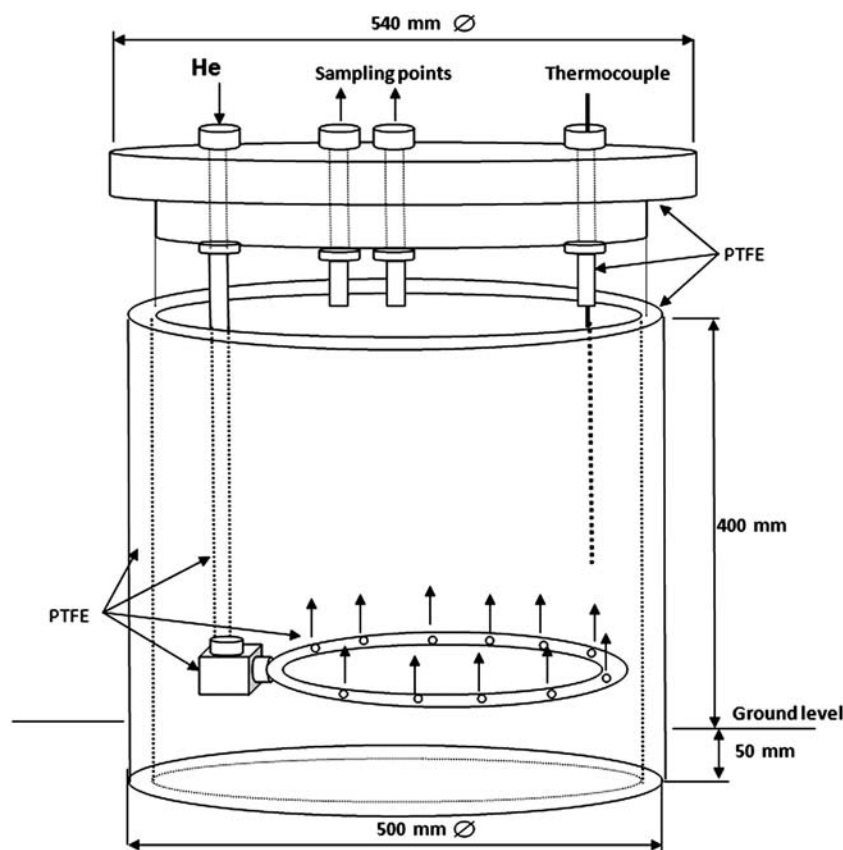


Fig. 2. Schematic diagram of the self-designed flux chamber used in the field investigation.

application of high flushing air flows and the underestimation of these rates due to an increase of the pressure inside the chamber. The two main objectives of the study are the evaluation of the performance of the chamber setup in typical measurement conditions and the determination of the emission rates of 60 VOC from a closed industrial landfill, which can be very useful in future studies as there are almost no published values from this type of landfills.

2. Materials and methods

2.1. Chemicals and materials

Standards of VOC with a purity of no less than 98% were obtained from Aldrich (Milwaukee, WI, USA), Merck (Darmstadt, Germany) and Fluka (Buchs, Switzerland). Methanol for gas chromatography (SupraSolv®)

with a purity $\geq 99.8\%$ was obtained from Merck (Darmstadt, Germany). Perkin Elmer glass tubes (Pyrex, 6 mm external diameter, 90 mm long), unsilanized wool, and Carbotrap (20/40 mesh), Carboxen X (40/60 mesh) and Carboxen 569 (20/45 mesh) adsorbents were purchased from Supelco (Bellefonte, PA, USA).

2.2. Site description

Can Planas industrial waste landfill is located approximately 15 km N of Barcelona, in Cerdanyola del Vallès (Catalonia, Spain), at $41^{\circ}29'25.69''\text{N}$ and $2^{\circ}7'14.36''\text{E}$, with the elevation ranging between 110 and 120 m above the sea level. Cerdanyola del Vallès has an annual average precipitation of 580 mm, and an annual average potential evapotranspiration of 1018.5 mm (calculated through the Thornthwaite method). The climate is Mediterranean, with mild winters ($7\text{--}10^{\circ}\text{C}$) and warm summers

Table 2
Sampling strategy.

Sampling point	FG-1	FG-2	FG-3	FG-4	FG-5
UTM-X	426,816.94	426,473.84	426,470.41	426,505.40	426,482.40
UTM-Y	4,593,657.52	4,593,695.92	4,593,575.51	4,593,822.51	4,593,909.51
4-7-2012		11:05–13:05 h			
5-7-2012	15:20–16:20 h			12:40–14:40 h	10:00–11:00 h
	15:20–17:20 h				10:00–12:00 h
9-7-2012			10:50–12:20 h	13:00–14:30 h	
11-7-2012	10:30–11:30 h		12:15–13:15 h		
	10:30–11:30 h		12:15–13:15 h		
13-7-2012		13:00–14:00 h		11:15–12:15 h	
		13:00–14:00 h			

UTM-X (ETRS89 zone 31N)UTM-Y (ETRS89 zone 31N).

Table 3
Emission rates ($\mu\text{g m}^{-2}\text{ day}^{-1}$) for the evaluated VOC in each sampling point.

Sampling day	5-7	5-7	11-7	11-7	4-7	13-7	13-7	9-7	11-7	11-7	5-7	9-7	13-7	5-7	5-7
Location	FG-1				FG-2			FG-3			FG-4			FG-5	
Temperature ($^{\circ}\text{C}$)	28.5	23	26	27	25	33	33.5	29.5	32	35	28	32	33	26	29
Relative humidity (%)	59	59	68	68	60	53	53	44	49	49	58	37	56	68	65
Pressure (hPa)	1008	1008	1016	1016	n.a.	1012	1012	1014	1016	1016	1018	1013	1013	1008	1009
Atmospheric pressure change ($\Delta\text{hPa h}^{-1}$)	-0.1	-0.2	0.9	0.9	n.a.	-0.8	-0.8	-0.1	-0.1	-0.1	-0.5	-0.7	-0.7	-0.3	-0.3
Compound	Superficial emission ($\mu\text{g m}^{-2}\text{ day}^{-1}$)														
<i>Alkanes</i>															
Cyclohexane	0.7	0.4	3.0	2.2	0.5	0.6	0.5	1.3	0.9	0.6	0.8	2.0	3.7	3.1	0.6
n-Decane	0.6	0.1	0.9	0.8	0.9	0.6	0.5	0.04	0.1	0.04	0.1	2.5	0.9	0.04	0.01
n-Hexane	2.3	1.0	5.3	3.9	2.1	0.7	2.0	1.4	0.7	5.5	1.5	4.2	5.2	11.6	4.3
n-Pentane	27.9	11.6	58.2	46.2	35.8	12.1	9.6	17.6	12.3	15.7	18.2	33.9	65.2	142	55.7
n-Tetradecane	80.3	18.5	52.8	52.6	9.6	105	95.9	39.3	85.1	50.5	20.3	125	76.6	16.0	6.1
<i>Aromatic hydrocarbons</i>															
1,2,3-Trimethylbenzene	0.3	0.1	1.0	1.0	0.1	0.3	0.3	0.4	0.5	0.5	0.1	0.4	2.3	0.4	0.1
1,2,4-Trimethylbenzene	2.3	0.4	5.5	5.4	0.8	2.0	1.8	1.6	2.7	2.5	0.8	1.7	9.3	3.1	0.8
1,3,5-Trimethylbenzene	0.7	0.1	1.3	1.0	0.2	0.2	0.1	0.5	0.6	0.5	0.2	0.4	1.7	0.6	0.1
1-Methylnaphthalene	0.5	0.1	0.5	0.6	0.1	0.4	0.4	0.9	0.7	0.6	0.2	0.6	0.6	0.2	0.1
2-Methylnaphthalene	1.1	0.2	1.2	1.0	0.2	0.9	0.8	1.5	1.6	1.5	0.5	1.8	1.7	0.1	0.1
Benzene	5.1	4.4	10.1	6.8	2.5	1.2	1.3	2.8	1.6	1.6	2.0	13.2	5.2	13.0	2.0
Ethylbenzene	1.3	0.2	7.4	5.8	0.4	1.6	1.6	1.8	2.4	3.2	0.5	2.6	10.1	2.3	0.4
m + p-Xylene	4.6	1.0	23.3	18.9	1.3	4.6	4.0	5.7	7.5	7.0	1.8	6.0	27.9	11.5	2.3
Naphthalene	0.9	0.2	1.1	0.9	0.3	0.9	0.9	1.0	1.1	1.2	0.3	1.5	2.0	0.4	0.2
n-Propylbenzene	0.2	0.1	0.5	0.5	0.01	0.1	0.1	0.1	0.1	0.04	0.1	0.2	0.7	0.1	0.01
o-Xylene	1.4	0.3	6.9	6.0	0.5	1.4	1.2	1.7	2.2	2.1	0.6	1.9	8.3	3.9	0.9
Styrene	1.0	0.1	4.6	4.0	0.2	0.8	0.7	0.5	1.2	2.7	0.1	0.5	9.4	0.8	0.1
Toluene	32.5	11.8	66.1	48.6	15.4	15.0	9.7	21.5	22.8	24.6	15.4	48.3	81.8	31.8	7.2
<i>Alcohols</i>															
1-Butanol	17.5	3.3	21.1	22.1	6.9	7.5	6.4	8.3	16.5	19.5	7.8	14.5	19.7	12.3	2.5
1-Propanol	0.3	0.3	2.6	2.6	0.9	1.3	1.4	2.1	1.3	1.7	1.1	2.1	3.0	0.2	0.2
Ethanol	77.5	36.3	38.8	36.5	4.6	6.2	8.1	12.6	12.7	19.8	9.1	15.0	29.4	27.7	7.5
Ethylhexanol	94.7	10.9	44.1	46.5	16.5	34.9	30.8	22.3	52.4	61.2	15.0	27.6	40.9	39.4	9.5
Isopropanol	0.02	0.003	0.03	0.03	n.d.	1.9	1.2	2.5	5.8	9.0	3.5	3.1	8.8	0.1	0.04
Phenol	16.4	1.8	12.8	7.8	7.8	19.4	20.7	10.4	16.5	13.6	4.3	51.2	19.0	40.4	7.9
<i>Ketones</i>															
Acetone	90.8	55.2	122	113	34.7	80.4	80.9	45.0	70.9	165	69.5	141	128	206	66.0
Cyclohexanone	3.1	0.5	6.6	8.0	2.9	3.9	3.6	2.5	7.3	9.0	1.9	2.8	8.1	3.3	0.8
Methylethylketone	0.6	0.5	9.2	2.3	0.7	2.0	3.5	0.03	0.04	0.1	1.9	11.4	26.9	0.9	0.3
Methylisobutylketone	3.4	0.9	3.3	2.9	1.0	1.2	0.9	1.0	1.3	1.5	1.1	1.1	4.3	4.5	1.0
<i>Halocarbons</i>															
1,1,1-Trichloroethane	0.2	0.1	0.4	0.4	0.2	0.3	0.3	0.2	0.3	0.3	0.1	0.3	0.3	0.3	0.1
1,2-Dichloroethane	1.1	0.4	1.1	0.9	1.0	1.1	1.1	1.6	0.8	0.9	0.3	3.1	1.2	0.9	0.2
Carbon tetrachloride	3.4	1.9	6.6	4.7	2.9	7.0	6.0	3.9	5.6	4.3	2.6	6.0	5.1	5.7	1.6
Chlorobenzene	n.d.	n.d.	1.1	0.9	0.01	0.1	0.03	0.02	0.2	0.1	0.01	0.1	0.4	n.d.	n.d.
Chloroform	4.1	1.9	11.5	7.3	2.6	2.0	4.7	1.3	1.3	20.4	1.4	2.5	3.5	7.1	1.2
Dichloromethane	1.9	0.6	5.6	3.8	0.7	0.6	0.4	2.6	2.7	2.0	0.9	2.3	7.1	5.7	2.3
o-Dichlorobenzene	0.1	n.d.	0.1	0.1	0.02	0.03	0.04	0.04	0.2	0.2	n.d.	0.1	0.1	n.d.	n.d.
p-Dichlorobenzene	0.04	0.01	0.1	0.1	0.01	0.1	0.1	0.1	0.1	0.1	0.01	0.1	0.2	0.04	0.01
Tetrachloroethylene	34.3	14.0	30.8	25.9	4.4	1.3	1.5	1.5	1.9	2.0	2.1	3.7	9.6	8.1	1.9
trans-1,2-Dichloroethylene	n.d.	n.d.	0.2	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	0.04	n.d.	n.d.	0.3	0.1
Trichloroethylene	0.4	0.2	1.5	1.0	0.4	0.3	0.3	0.7	0.5	0.5	0.1	0.8	1.5	0.6	0.1
<i>Aldehydes</i>															
Benzaldehyde	0.9	0.2	1.2	1.0	0.4	0.9	1.2	2.8	2.9	3.6	0.5	4.8	2.9	0.2	0.03
Decanal	309	57.2	222	176	90.6	488	379	206	429	634	123	392	295	69.6	30.7
Heptanal	11.5	2.0	6.3	4.9	4.1	12.0	10.3	4.3	10.0	11.7	3.7	12.3	8.3	3.0	1.0
Hexanal	18.5	2.2	6.7	6.3	5.8	7.2	5.1	6.3	8.8	9.7	5.0	14.9	5.6	6.6	1.6
Nonanal	323	69.9	234	210	119	671	590	197	389	672	123	432	442	105	44.3
Octanal	59.0	10.6	41.8	37.8	20.0	63.8	63.6	31.5	57.0	77.1	18.1	48.6	79.9	18.3	7.0
<i>Esters</i>															
Butyl acetate	1.0	0.3	4.9	3.7	0.5	2.2	1.9	1.8	3.8	3.4	0.3	2.9	2.7	1.5	0.3
Ethyl acetate	5.5	2.0	15.2	9.3	2.3	3.2	4.5	5.2	4.0	5.5	3.5	8.5	6.9	14.3	4.2
Methyl acetate	1.4	0.6	3.5	3.0	0.3	1.9	1.5	0.5	1.5	1.4	0.5	2.5	1.6	1.5	0.5
<i>Terpenoids</i>															
α -Pinene	1.3	0.5	3.5	2.7	0.5	3.8	3.1	1.1	2.9	2.5	0.4	3.3	13.2	1.4	0.3
β -Pinene	1.5	0.3	2.4	2.0	0.1	2.1	1.8	0.5	1.4	1.3	0.4	0.6	9.8	1.5	0.3
D-Limonene	1.0	0.1	1.1	0.9	0.3	1.0	0.5	1.8	12.3	10.5	1.2	0.8	2.8	0.9	0.2
p-Cymene	0.1	0.01	0.4	0.6	0.04	0.3	0.4	0.9	1.2	0.6	0.2	0.7	2.7	1.0	0.2

Table 3 (continued)

Sampling day	5-7	5-7	11-7	11-7	4-7	13-7	13-7	9-7	11-7	11-7	5-7	9-7	13-7	5-7	5-7
Location	FG-1				FG-2			FG-3			FG-4			FG-5	
Temperature (°C)	28.5	23	26	27	25	33	33.5	29.5	32	35	28	32	33	26	29
Relative humidity (%)	59	59	68	68	60	53	53	44	49	49	58	37	56	68	65
Pressure (hPa)	1008	1008	1016	1016	n.a.	1012	1012	1014	1016	1016	1018	1013	1013	1008	1009
Atmospheric pressure change (Δ hPa h ⁻¹)	-0.1	-0.2	0.9	0.9	n.a.	-0.8	-0.8	-0.1	-0.1	-0.1	-0.5	-0.7	-0.7	-0.3	-0.3
Compound	Superficial emission ($\mu\text{g m}^{-2} \text{day}^{-1}$)														
<i>Ethers</i>															
tert-Butyl ethyl ether	8.7	2.6	15.9	8.3	3.4	4.6	5.4	5.2	3.7	4.9	4.5	12.0	14.1	22.7	8.5
tert-Butyl methyl ether	0.3	0.1	4.8	4.1	0.2	0.2	0.1	0.1	0.5	0.6	0.1	0.3	1.4	0.8	0.4
<i>Nitrogenated compounds</i>															
Acetonitrile	n.d.	n.d.	n.d.	n.d.	n.d.	0.03	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cyclohexane isocyanato	0.4	0.1	0.5	0.5	0.6	3.0	1.4	2.0	2.8	3.1	0.2	0.8	1.1	0.6	0.4
Cyclohexane isothiocyanato	0.03	0.01	0.02	0.02	0.01	0.04	0.04	0.03	0.1	0.1	0.01	0.03	0.03	0.01	0.004
<i>Sulfur compounds</i>															
Carbon disulfide	1.9	3.7	1.3	0.9	0.6	0.2	0.8	0.2	0.2	0.4	0.1	6.0	0.2	1.9	1.4
<i>Furans</i>															
Tetrahydrofuran	n.d.	n.d.	0.9	0.3	0.8	0.5	1.7	0.5	n.d.	24.8	0.1	0.5	3.9	0.8	0.3
<i>Carboxylic acids</i>															
Acetic acid	352	54.7	461	473	57.7	251	210	131	417	662	99	369	486	86.3	19.9

n.a.: not available.

n.d.: not detected.

(21–26 °C). The total area and volume of the landfill (a previous clay quarry) are approximately 18 ha and 2,450,000 m³, respectively, consisting of three main buckets (which had been formed as a result of extractive activity): North, North-East and South buckets. The landfill started operating in 1982 and was closed in 1995, having experienced waste disposal activities at varying rates. The site is based on a silt-clay layer with a main composition of 61–64% of phyllosilicates, 12–23% of quartz and 8–22% of calcite (IDOM, 2008a). Before the operation of the landfill site, a low permeability silty clay layer was pressed tightly to prevent leachate movement. The final cover of the landfill (approximately 1 m clay, 20 cm gravel Ø 7 cm, 1 m soil, 20 cm topsoil) was settled in 1994 (IDOM, 2008a, 2008b) and was spontaneously vegetated with different herbs and grasses; probably originating from weed seed, as no vegetation was planted. The leaching liquid is collected and discharged out into an enclosed leachate collection pool. Based on characterization studies, the type of wastes buried in the studied landfill consisted mainly of clay and silt soils (inert residues), construction and demolition wastes (inert residues), industrial waste (nonspecial and special residues) and miscellaneous wastes, being a co-disposal facility (Table 1, Fig. 1) (IDOM, 2008a). Inert residues do not experiment significant physical, chemical and/or biological transformations. Nonspecial residues do not present environmental, health and/or natural resources risks, and cannot be valorized. Finally, special residues need a specific treatment and a periodical control. They are potentially hazardous to the environment, human health and/or the natural resources. It has to be taken into account that different composition residues could be superimposed in the same landfill bucket, thus the VOC source material is notably heterogeneous. To facilitate generated landfill gases flaring, two vertical gas chimneys were built in the South bucket. The landfill is not equipped with a gas recovery system.

Waste in the studied area was 17–30 years old when emission testing began, and the cover was fully vegetated at the time of the field campaign.

2.3. Flux chamber measurements

A cylindrical air flux chamber was used to measure VOC surface emissions (Fig. 2). The flux chamber system, manufactured in our laboratory considering a series of design and operation implications and

recommendations (Gao and Yates, 1998; Hudson and Ayoko, 2008; Rochette, 2011; D. Parker et al., 2013), consisted of an internally polytetrafluoroethylene (PTFE) coated chamber, a compressed He tank, a flow meter, a PTFE He distributor inside the chamber, a temperature probe and two PTFE sampling ports. The surface area and the volume of the flux chamber are 1810 cm² and 86.4 l, respectively. The volume/area ratio (cm³ cm⁻²) is 48. Air passes from the gas tank, through the flow meter, to the flux chamber at a fixed steady rate (100 or 200 ml min⁻¹), according to sampling conditions (1 or 2 samples taken simultaneously). The presented flux chamber is notably inexpensive, portable and can be removed in its entirety after each measurement (Fourie and Morris, 2004).

The flux chamber was inserted into the topsoil to a depth of 5 cm gently pressing the open edge of the cylinder, ensuring a good seal around the base of the chamber, and allowed to equilibrate for 15 min before each measurement. This equilibration time was established to avoid sampling errors derived from the pressure disturbance generated by the disposition of the sampling device (Pihlatie et al., 2013). Furthermore, to avoid an initial pressure increase, sampling valves were open during equilibration. Moreover, as the same flux of He was inserted into the chamber than the sampling flow was removed, neither a pressure increase nor vacuum in the chamber headspace was expected.

The chamber was adequately isolated from environmental conditions such as insolation; hence, the outside construction was opaque and reflective to reduce its capacity for heat adsorption and transfer, and was shaded when sampling under intense sun to avoid increases in emission rates at midday (Park and Shin, 2001; Kolari et al., 2012). Additionally, the chamber temperature was monitored to verify that it was not increasing relative to the outside temperature. Vegetation inside the flux chamber was removed so to not interfere with the sampling and avoid overestimation/underestimation of the measured emission rates (Hudson and Ayoko, 2008).

Surface emission sampling was performed in the summer season, July 2012, characterized by hot and dry conditions. Summer season was chosen for sampling as the high temperatures expected for this period of the year assured us the worst possible scenario regarding to VOC emissions. The selected sampling points (Fig. 1) were evaluated in triplicate, some replicate samples were taken during the same day, and others were sampled in different days (Table 2).

Table 4

Average \pm SD (%CV), minimum and maximum VOC emission rates (of the $n = 15$ measurements) obtained through *Global* methodology.

Compound	Global ($\mu\text{g m}^{-2} \text{day}^{-1}$)				
	Average	SD	%CV	Min	Max
<i>Alkanes</i>					
Cyclohexane	1.4	0.4	29	0.6	2.4
<i>n</i> -Decane	0.5	0.2	43	0.2	0.9
<i>n</i> -Hexane	3.8	1.0	26	1.6	5.9
<i>n</i> -Pentane	41.7	10.4	25	21.5	63.7
<i>n</i> -Tetradecane	54.9	13.6	25	18.8	82.2
Total alkanes	102	19	18	42.6	155
<i>Aromatic hydrocarbons</i>					
1,2,3-Trimethylbenzene	0.5	0.2	43	0.2	0.9
1,2,4-Trimethylbenzene	2.6	0.9	35	0.9	4.5
1,3,5-Trimethylbenzene	0.5	0.2	34	0.2	0.9
1-Methylnaphthalene	0.4	0.1	16	0.2	0.5
2-Methylnaphthalene	0.9	0.2	17	0.5	1.1
Benzene	4.9	1.5	31	2.2	8.3
Ethylbenzene	2.6	1.1	40	0.7	4.9
<i>m</i> + <i>p</i> -Xylene	8.1	3.1	38	2.4	14.9
Naphthalene	0.8	0.2	20	0.4	1.1
<i>n</i> -Propylbenzene	0.2	0.1	44	0.04	0.3
<i>o</i> -Xylene	2.5	0.9	37	0.8	4.5
Styrene	1.7	1.0	58	0.2	3.7
Toluene	28.8	7.2	25	13.1	43.9
Total aromatic hydrocarbons	54.6	15.3	28	21.8	89.7
<i>Alcohols</i>					
1-Butanol	11.7	2.3	19	5.7	16.2
1-Propanol	1.3	0.3	22	0.7	1.9
Ethanol	20.8	4.5	21	14.0	32.5
Ethylhexanol	34.8	7.9	23	14.8	54.2
Isopropanol	2.5	0.8	32	1.4	4.0
Phenol	17.6	5.4	30	6.4	29.0
Total alcohols	88.7	17.2	19	43.0	137.7
<i>Ketones</i>					
Acetone	101	20	20	54.1	143
Cyclohexanone	4.1	1.0	25	1.7	6.4
Methylethylketone	3.8	2.2	57	0.7	8.1
Methylisobutylketone	2.0	0.5	26	1.0	3.0
Total ketones	111	22	20	57.4	161
<i>Halocarbons</i>					
1,1,1-Trichloroethane	0.23	0.04	17	0.1	0.3
1,2-Dichloroethane	1.0	0.3	26	0.5	1.6
Carbon tetrachloride	4.5	0.7	16	2.6	6.2
Chlorobenzene	0.3	0.1	66	0.2	0.3
Chloroform	4.7	2.1	44	1.8	9.4
Dichloromethane	2.7	0.7	28	1.2	4.3
<i>o</i> -Dichlorobenzene	0.05	0.01	33	0.03	0.1
<i>p</i> -Dichlorobenzene	0.06	0.02	30	0.02	0.1
Tetrachloroethylene	8.1	1.8	22	4.2	11.7
<i>trans</i> -1,2-Dichloroethylene	0.05	0.03	47	0.1	0.1
Trichloroethylene	0.6	0.2	29	0.2	0.9
Total halocarbons	22.2	4.3	20	11.0	35.1
<i>Aldehydes</i>					
Benzaldehyde	1.5	0.4	25	0.8	2.2
Decanal	251	57	23	101	379
Heptanal	6.7	1.4	20	3.0	10.1
Hexanal	7.1	1.6	23	4.0	11.4
Nonanal	299	72	24	111	443
Octanal	40.6	8.4	21	17.5	59.6
Total aldehydes	606	137	23	237	904
<i>Esters</i>					
Butyl acetate	2.0	0.5	26	0.6	3.1
Ethyl acetate	6.3	1.5	23	3.2	9.6
Methyl acetate	1.4	0.3	25	0.5	2.1
Total esters	9.7	2.2	23	4.3	14.8
<i>Terpenoids</i>					
α -Pinene	2.6	1.2	45	0.6	5.0
β -Pinene	1.7	0.9	55	0.3	3.4
<i>D</i> -Limonene	2.3	0.9	40	0.7	3.6
<i>p</i> -Cymene	0.6	0.2	37	0.2	1.2
Total terpenoids	7.3	2.7	38	1.7	13.2

Table 4 (continued)

Compound	Global ($\mu\text{g m}^{-2} \text{day}^{-1}$)				
	Average	SD	%CV	Min	Max
<i>Ethers</i>					
<i>tert</i> -Butyl ethyl ether	8.8	1.9	22	4.5	12.7
<i>tert</i> -Butyl methyl ether	0.8	0.5	56	0.2	1.5
Total ethers	9.6	2.2	23	4.7	14.2
<i>Nitrogenated compounds</i>					
Acetonitrile	0.005	0.003	73	0.006	0.008
Cyclohexane isocyanato	1.2	0.2	20	0.7	1.6
Cyclohexane isothiocyanato	0.024	0.004	18	0.01	0.03
Total nitrogenated	1.2	0.2	20	0.7	1.7
<i>Sulfur compounds</i>					
Carbon disulfide	1.3	0.6	47	0.5	2.6
<i>Furans</i>					
Tetrahydrofuran	2.4	2.4	100	0.3	6.4
<i>Carboxylic acids</i>					
Acetic acid	256	67	26	72.3	392
Total emissions (g day^{-1})	237	48	20	93	391

VOC were dynamically collected by coupling to the sampling port custom packed glass multi-sorbent cartridge tubes (Carbotrap 20/40, 70 mg; Carbopack X 40/60, 100 mg and Carboxen 569 20/45, 90 mg) connected to AirChek 2000 SKC pumps at a flow of 100 ml min^{-1} during 1 to 2 h. The PTFE sampling tube length (between the sampling port and the sampling tube) was as short as possible to avoid potential negative effects of the tube length on the measured concentrations (Kolari et al., 2012). Collected air samples were analyzed by thermal desorption and gas chromatography–mass spectrometry detector (TD–GC/MSD) (Ribes et al., 2007). This methodology has been used in previous studies to identify and determine a wide range of VOC in ambient air (Gallego et al., 2009, 2011).

2.4. Analytical instrumentation

The analysis of VOC was performed by automatic thermal desorption (ATD) coupled with capillary gas chromatography (GC)/mass spectrometry detector (MSD), using a Perkin Elmer ATD 400 (Perkin Elmer, Boston, Massachusetts, USA) and a Thermo Quest Trace 2000 GC (ThermoQuest, San Jose, California, USA) fitted with a Thermo Quest Trace Finnigan MSD.

The methodology is described in the literature (Ribes et al., 2007; Gallego et al., 2009). Thermal primary desorption of the sampling tubes was carried out at 300°C , with a helium flow rate of 50 ml min^{-1} for 10 min. The double-split applied to the TD system (cold trap inlet and outlet splits of 4 ml min^{-1} and 7 ml min^{-1} , respectively) allowed 12% of the tube analytes to reach the MS detector. The cold trap (15 mg Tenax TA and 15 mg Carbotrap) was maintained at -30°C . After primary desorption, the cold trap was rapidly heated from -30°C to 300°C (secondary desorption), and maintained at this temperature for 10 min. Analytes were then injected onto the capillary column (DB-624, $60 \text{ m} \times 0.25 \text{ mm} \times 1.4 \mu\text{m}$) via a transfer line heated at 200°C . The column oven temperature started at 40°C for 1 min, increased to 230°C at a rate of 6°C min^{-1} and then was maintained at 230°C for 5 min. Helium (99.999%) carrier gas flow in the analytical column was approximately 1 ml min^{-1} (1.4 bar).

Electron impact source was obtained with electron energy of 70 eV. Mass spectral data were acquired over a mass range of 20–300 amu. Quantification of samples was conducted by the external standard method. Limits of detection (LOD), determined by applying a signal-to-noise ratio of 3, range from 0.001 to 10 ng. The studied compounds show repeatabilities (% relative standard deviation values) $\leq 25\%$ (Ribes et al., 2007), accomplishing the EPA performance criteria (US EPA, 1999).

Table 5

Average \pm SD (%CV), minimum and maximum VOC emission rates (of the $n = 15$ measurements) obtained through Kriging methodology.

Compound	Kriging ($\mu\text{g m}^{-2} \text{day}^{-1}$)				
	Average	SD	%CV	Min	Max
<i>Alkanes</i>					
Cyclohexane	0.6	0.2	31	0.3	1.0
<i>n</i> -Decane	0.2	0.1	36	0.1	0.4
<i>n</i> -Hexane	1.6	0.4	27	0.8	2.7
<i>n</i> -Pentane	18.5	5.1	28	10.6	31.9
<i>n</i> -Tetradecane	21.3	6.6	31	6.6	36.3
Total alkanes	42.1	8.3	20	18.4	72.3
<i>Aromatic hydrocarbons</i>					
1,2,3-Trimethylbenzene	0.2	0.1	42	0.1	0.4
1,2,4-Trimethylbenzene	1.0	0.3	34	0.4	1.9
1,3,5-Trimethylbenzene	0.2	0.1	34	0.1	0.3
1-Methylnaphthalene	0.14	0.03	19	0.1	0.2
2-Methylnaphthalene	0.3	0.1	22	0.1	0.4
Benzene	2.0	0.7	34	1.0	3.8
Ethylbenzene	0.9	0.4	40	0.2	2.0
<i>m</i> + <i>p</i> -Xylene	3.0	1.1	38	0.9	6.2
Naphthalene	0.3	0.1	22	0.1	0.5
<i>n</i> -Propylbenzene	0.06	0.02	43	0.01	0.1
<i>o</i> -Xylene	1.0	0.3	36	0.3	1.9
Styrene	0.6	0.3	58	0.1	1.4
Toluene	10.7	2.7	25	5.2	18.3
Total aromatic hydrocarbons	20.3	5.7	28	8.5	37.5
<i>Alcohols</i>					
1-Butanol	4.2	0.8	19	2.4	6.5
1-Propanol	0.5	0.1	22	0.3	0.7
Ethanol	7.7	1.7	22	5.5	13.4
Ethylhexanol	13.0	2.9	23	6.4	22.5
Isopropanol	0.7	0.2	33	0.5	1.3
Phenol	7.4	2.3	31	2.9	13.6
Total alcohols	33.5	7.0	21	18.1	58.1
<i>Ketones</i>					
Acetone	40.2	8.5	21	24.1	62.5
Cyclohexanone	1.5	0.3	22	0.8	2.5
Methylethylketone	1.5	0.8	52	0.3	3.4
Methylisobutylketone	0.8	0.2	28	0.4	1.4
Total ketones	44.0	9.2	21	25.7	69.7
<i>Halocarbons</i>					
1,1,1-Trichloroethane	0.09	0.02	18	0.1	0.1
1,2-Dichloroethane	0.4	0.1	23	0.3	0.7
Carbon tetrachloride	1.8	0.3	19	1.1	2.9
Chlorobenzene	0.05	0.04	68	0.1	0.2
Chloroform	1.7	0.5	31	0.8	3.5
Dichloromethane	1.0	0.3	28	0.5	1.8
<i>o</i> -Dichlorobenzene	0.015	0.004	28	0.02	0.03
<i>p</i> -Dichlorobenzene	0.02	0.01	31	0.01	0.04
Tetrachloroethylene	3.1	0.7	22	1.7	5.1
<i>trans</i> -1,2-Dichloroethylene	0.03	0.01	46	0.04	0.1
Trichloroethylene	0.2	0.1	29	0.1	0.4
Total halocarbons	8.4	1.6	19	4.7	14.7
<i>Aldehydes</i>					
Benzaldehyde	0.5	0.1	28	0.2	0.8
Decanal	93	25	27	39	158
Heptanal	2.6	0.6	22	1.3	4.4
Hexanal	2.7	0.6	22	1.7	4.8
Nonanal	120	35	29	45	196
Octanal	15.6	3.5	23	7.2	25.2
Total aldehydes	235	64	27	94.2	389
<i>Esters</i>					
Butyl acetate	0.7	0.2	28	0.2	1.3
Ethyl acetate	2.6	0.7	26	1.4	4.4
Methyl acetate	0.5	0.1	26	0.2	1.0
Total esters	3.8	0.9	24	1.8	6.6
<i>Terpenoids</i>					
α -Pinene	1.0	0.4	43	0.2	2.1
β -Pinene	0.7	0.3	51	0.1	1.5
δ -Limonene	0.6	0.2	30	0.2	1.0
<i>p</i> -Cymene	0.2	0.1	39	0.1	0.5
Total terpenoids	2.5	0.9	38	0.6	5.1

Table 5 (continued)

Compound	Kriging ($\mu\text{g m}^{-2} \text{day}^{-1}$)				
	Average	SD	%CV	Min	Max
<i>Ethers</i>					
<i>tert</i> -Butyl ethyl ether	3.7	0.9	24	2.2	6.0
<i>tert</i> -Butyl methyl ether	0.3	0.2	53	0.1	0.6
Total ethers	4.0	0.9	24	2.2	6.6
<i>Nitrogenated compounds</i>					
Acetonitrile	0.003	0.002	73	0.01	0.01
Cyclohexane isocyanato	0.4	0.1	32	0.2	0.7
Cyclohexane isothiocyanato	0.009	0.002	24	0.01	0.01
Total nitrogenated	0.4	0.1	31	0.2	0.8
<i>Sulfur compounds</i>					
Carbon disulfide	0.5	0.2	40	0.3	1.1
<i>Furans</i>					
Tetrahydrofuran	0.6	0.4	71	0.1	1.7
<i>Carboxylic acids</i>					
Acetic acid	87	21	24	28	146
Total emissions (g day^{-1})	77	17	22	42	145

2.5. Data analysis

2.5.1. Emission rate calculations

The emission rates ($\mu\text{g m}^{-2} \text{day}^{-1}$) were calculated from the product of the concentration of VOC inside the chamber ($\mu\text{g m}^{-3}$) and the chamber volume (m^3). The amount of VOC obtained (μg) was referred to the surface area (m^2) and the sampling time (days).

2.5.2. Data treatment

Data treatment, statistical and graphical analysis was undertaken using Microsoft Excel™ 2007, IBM Spss Statistics Version 20 (2011) and Matlab v.7 (The MathWorks, Inc.). Specific Matlab programs were developed to treat the experimental data, to compute all the possible data combinations (tributary method), to make the data interpolations (kriging method) and to obtain the graphical output for the three methods tested. Kolmogorov–Smirnov (K–S) test was used to check normal distribution of the experimental data. F-Snedecor test was used to evaluate significant correlations between the obtained data. The data used for the correlation analysis were the measured emission rates obtained at each individual measuring point at each measuring time (Table 3).

3. Results and discussion

3.1. VOC emission rates

The emission rates of 60 different VOC were calculated for each sampling point ($n = 3$ samples in each point) in an effort to characterize VOC surface emissions in a closed industrial landfill. Experimentally calculated VOC superficial emission rates for all sampling points are presented in Table 3. From sample to sample, minor variations in the VOC emission rates were found. The data sets obtained for each VOC were normally distributed (Kolmogorov–Smirnov (K–S) test; $p \leq 0.05$), indicating that the emission rates for each compound in the five studied points were considerably homogeneous, even though the heterogeneity of the industrial waste was present in the investigated landfill site (Table 1). This similarity in emission rates may have been induced by the stabilization of the landfill since its closing date (1995). It has to be noted; however, that isopropanol and methylethylketone presented lower values in FG-1 and FG-3, respectively. Furthermore, tetrachloroethylene presented higher surface emission rates in FG-1.

The experimentally found emission rates are comparable and of the same order of magnitude than the values obtained in previous studies

Table 6

Average \pm SD (%CV), minimum and maximum VOC emission rates (of the $n = 15$ measurements) obtained through *Tributary area* methodology.

Compound	Tributary area ($\mu\text{g m}^{-2} \text{day}^{-1}$)				
	Average	SD	%CV	Min	Max
<i>Alkanes</i>					
Cyclohexane	1.6	0.5	33	0.6	2.7
<i>n</i> -Decane	0.5	0.2	47	0.1	0.9
<i>n</i> -Hexane	4.3	1.1	27	1.9	6.6
<i>n</i> -Pentane	48.9	13.2	27	24.4	74.6
<i>n</i> -Tetradecane	49.8	12.9	26	16.9	76.9
Total alkanes	105	22	21	43.9	162
<i>Aromatic hydrocarbons</i>					
1,2,3-Trimethylbenzene	0.5	0.3	48	0.1	1.0
1,2,4-Trimethylbenzene	2.8	1.1	40	0.8	5.0
1,3,5-Trimethylbenzene	0.6	0.2	38	0.2	1.0
1-Methylnaphthalene	0.4	0.1	20	0.2	0.5
2-Methylnaphthalene	0.8	0.2	22	0.4	1.0
Benzene	5.8	1.9	33	2.6	9.9
Ethylbenzene	2.8	1.3	46	0.5	5.6
<i>m</i> + <i>p</i> -Xylene	9.1	4.0	44	2.0	17.4
Naphthalene	0.8	0.2	24	0.3	1.1
<i>n</i> -Propylbenzene	0.2	0.1	45	0.04	0.3
<i>o</i> -Xylene	2.8	1.2	42	0.7	5.3
Styrene	1.8	1.1	62	0.2	4.1
Toluene	31.6	9.1	29	12.2	50.5
Total aromatic hydrocarbons	60.1	19.3	32	20.1	103
<i>Alcohols</i>					
1-Butanol	12.0	2.8	24	5.0	17.1
1-Propanol	1.3	0.4	31	0.6	1.9
Ethanol	24.8	6.1	25	16.6	39.7
Ethylhexanol	35.0	10.2	29	13.3	57.9
Isopropanol	1.9	0.7	35	1.1	3.2
Phenol	18.0	6.3	35	5.5	30.9
Total alcohols	93.0	21.9	24	42.1	151
<i>Ketones</i>					
Acetone	106	22	21	57.8	148
Cyclohexanone	3.9	1.1	30	1.4	6.4
Methyl ethyl ketone	4.3	2.6	59	0.7	9.4
Methyl isobutyl ketone	2.2	0.6	29	1.0	3.5
Total ketones	117	24	21	60.8	167
<i>Halocarbons</i>					
1,1,1-Trichloroethane	0.2	0.1	21	0.1	0.3
1,2-Dichloroethane	1.0	0.3	30	0.4	1.6
Carbon tetrachloride	4.3	0.8	19	2.3	6.2
Chlorobenzene	0.2	0.2	77	0.3	0.4
Chloroform	4.6	1.6	35	2.0	8.7
Dichloromethane	3.0	0.9	31	1.2	5.1
<i>o</i> -Dichlorobenzene	0.04	0.01	33	0.03	0.1
<i>p</i> -Dichlorobenzene	0.06	0.02	35	0.02	0.1
Tetrachloroethylene	10.7	2.5	24	5.4	15.1
<i>trans</i> -1,2-Dichloroethylene	0.07	0.03	50	0.1	0.1
Trichloroethylene	0.6	0.2	35	0.2	1.0
Total halocarbons	25.0	5.5	22	12.1	38.7
<i>Aldehydes</i>					
Benzaldehyde	1.3	0.4	32	0.5	2.0
Decanal	211	46	22	84.5	321
Heptanal	6.1	1.4	23	2.6	9.5
Hexanal	7.0	2.2	31	3.5	12.4
Nonanal	253	56	22	94.3	370
Octanal	36.7	8.4	23	14.7	55.6
Total aldehydes	515	111	21	200	770
<i>Esters</i>					
Butyl acetate	1.9	0.7	34	0.5	3.2
Ethyl acetate	7.1	2.0	29	3.1	11.2
Methyl acetate	1.5	0.4	28	0.5	2.3
Total esters	10.4	3.0	29	4.1	16.7
<i>Terpenoids</i>					
α -Pinene	2.6	1.3	50	0.5	5.1
β -Pinene	1.8	1.0	59	0.3	3.7
<i>D</i> -Limonene	1.7	0.5	32	0.5	2.6
<i>p</i> -Cymene	0.6	0.3	43	0.2	1.2
Total terpenoids	6.6	2.8	43	1.5	12.6

Table 6 (continued)

Compound	Tributary area ($\mu\text{g m}^{-2} \text{day}^{-1}$)				
	Average	SD	%CV	Min	Max
<i>Ethers</i>					
<i>tert</i> -Butyl ethyl ether	10.0	2.5	25	4.7	14.9
<i>tert</i> -Butyl methyl ether	1.0	0.6	63	0.2	2.0
Total ethers	11.0	2.9	26	4.9	17.0
<i>Nitrogenated compounds</i>					
Acetonitrile	0.003	0.002	73	0.003	0.004
Cyclohexane isocyanato	0.9	0.2	18	0.5	1.2
Cyclohexane isothiocyanato	0.020	0.004	18	0.01	0.03
Total nitrogenated	0.9	0.2	18	0.5	1.2
<i>Sulfur compounds</i>					
Carbon disulfide	1.6	0.7	46	0.7	3.1
<i>Furans</i>					
Tetrahydrofuran	1.6	1.3	83	0.3	4.2
<i>Carboxylic acids</i>					
Acetic acid	247	67	27	63.9	370
Total emissions (g day^{-1})	222	46	21	95.6	366

evaluating closed landfills (3–5 years) with vegetated covers (Schultz et al., 2003, 2008; Barlaz et al., 2004). In these studies, negative emission fluxes were found for several VOC depending on the sampling site, indicating an inward gradient from the atmosphere to the soil. In the present study, however, all emission rates determined were positive.

In order to check the consistency of the obtained results, three statistical methods were used to present a complete statistical treatment of the experimental data, taking into account that there are several spatial variables that can influence VOC emissions all over the landfill, such as the type of waste buried, the different time elapsed since the burying of the waste in each bucket, the depth of the bucket, the type of soil under and over the buried waste, and the possible presence of underground water streams.

Therefore, to assess the average \pm SD, maximum and minimum emissions of VOC over the surface area of the studied landfill, the data measured at each sampling point were converted through three different ways: *Global*, *Kriging*, and *Tributary area* methodologies. The average \pm SD, minimum and maximum emission rates obtained from the three procedures are presented in Tables 4–6. Maximum and minimum *Global* values from all individual data ($n = 15$ for each studied VOC, Table 2) were obtained averaging the maximum and minimum experimentally determined values at each point ($n = 3$ samples in each point), respectively. Average *Global* values were obtained averaging the five average values obtained in each sampling point ($n = 3$ samples in each point). *Kriging* data and *Tributary area* data were obtained using specific developed Matlab software that takes into account all the 216 combinations ($4 \times 3 \times 3 \times 3 \times 2$ samples from FG-1, FG-2, FG-3, FG-4 and FG-5, respectively, Table 2) of the different experimental emission data obtained for each one of the 73 chemical species (individual compounds, families, and TVOC) at the five sampling points. For the *Kriging* data, spatial interpolation (triangle-based linear interpolation method) was used. For *Tributary area* data, the average of the combinations was used. The calculation of the SD and %CV parameters was done using all the possibilities of emission for each point for the *Tributary area* and *Kriging* methods.

Global calculated minimum, maximum and average \pm SD individual VOC emission rate values range from 0.01–111 $\mu\text{g m}^{-2} \text{day}^{-1}$, 0.01–443 $\mu\text{g m}^{-2} \text{day}^{-1}$ and 0.005 ± 0.003 – 299 ± 72 $\mu\text{g m}^{-2} \text{day}^{-1}$, respectively. *Kriging* calculated minimum, maximum and average \pm SD emission rates range from 0.01–45 $\mu\text{g m}^{-2} \text{day}^{-1}$, 0.01–196 $\mu\text{g m}^{-2} \text{day}^{-1}$ and 0.003 ± 0.002 – 120 ± 35 $\mu\text{g m}^{-2} \text{day}^{-1}$, respectively. Finally, *Tributary area* calculated minimum, maximum and average \pm SD values range from 0.003–94 $\mu\text{g m}^{-2} \text{day}^{-1}$, 0.004–370 $\mu\text{g m}^{-2} \text{day}^{-1}$ and 0.003 ± 0.002 –

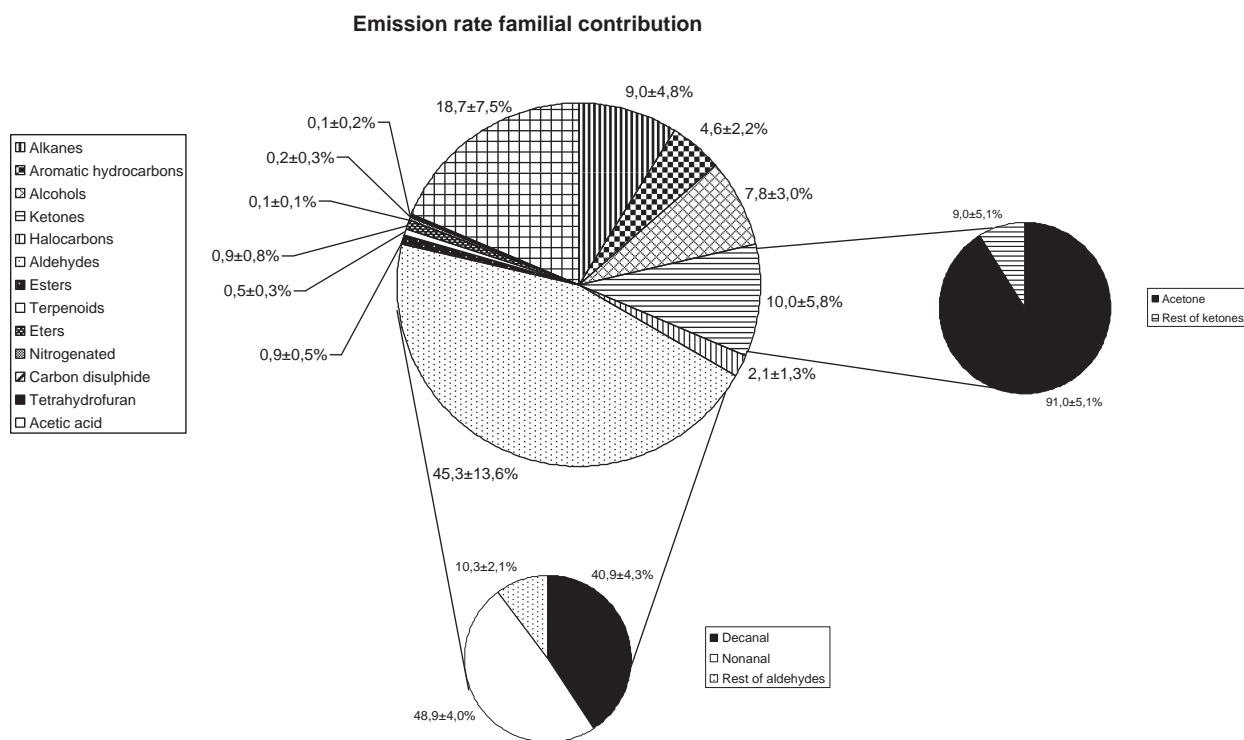


Fig. 3. Emission rate familial contribution.

$253 \pm 56 \mu\text{g m}^{-2} \text{day}^{-1}$, respectively. *Global* and *Tributary area* values are considerably similar; however, *Kriging* values are lower, as it has been observed in previous studies (Fourie and Morris, 2004), due to the fact that the *Kriging* methodology is based on the assumption of null VOC emissions in the borders of the landfill.

All three conversion methods used had remarkable associated statistical data (standard deviation (SD) and coefficient of variation between the data (%CV)), with constant and relatively low values. %CV values were very similar among the three computing procedures, with average values between 33% and 36%. Previous works reported highly variable VOC emission fluxes, both spatially and temporally (Scheutz et al., 2003, 2008; Barlaz et al., 2004). It has to be considered, however, that these studies were conducted between 3 and 5 years after the landfills were finally covered, and the present study started at least after 17 years of the final closure of the landfill. Higher stabilization time can have favored these lower variation rates among samples in all the landfill. Nevertheless, these low %CV values indicate that the sampling methodology is sound.

3.1.1. VOC familial contribution to the emission profile

Aldehydes, acetic acid, ketones, alkanes and alcohols are the families that dominated the emission profile, comprising 45%, 19%, 10%, 9% and 8%, respectively, of the total emissions (Fig. 3). Among aldehydes and ketones, nonanal and decanal, and acetone, respectively, are the individual compounds that contribute more to the total emission rate. These VOC groups are the major families generally found in waste treatment facilities and in landfill biogas and their generation can be associated to the presence of heterogeneous waste matter at varied decomposition degrees under oxidizing conditions (Tassi et al., 2009; Chiriac et al., 2011). These oxygen-bearing families (aldehydes, ketones and organic acids) are oxidized products of hydrocarbons, and therefore their generation is triggered at aerobic conditions. As it has been observed in previous studies, their presence in landfill gas is higher in samples taken close to the air–soil interface, namely in the surface of the landfill site (Tassi et al., 2009).

Table 7 shows VOC weighted average contribution in respect to the total emission (TVOC) profile (each VOC contribution to the sum of all VOC in each sample, $n = 15$), and their weighted average contribution in respect to its familial emission profile (each VOC contribution to its family in each sample, $n = 15$). Several VOC are the main contributors of the studied families (e.g. *n*-pentane and *n*-tetradecane in alkanes, *m* + *p*-xylene and toluene in aromatic hydrocarbons). Additionally, the moderate standard deviations found in this parameter indicate a similar behavior of each compound in respect to its family in all the area of the studied landfill.

3.1.2. Emission rate correlations

The relationships between the measured VOC emission rates were examined statistically using the correlation analysis. The data used for the correlation analysis were the measured emission rates obtained at each individual measuring point at each measuring time (Table 3). Several families correlated significantly between each other (F-Snedecor, $p \leq 0.001$): alkanes vs. ketones ($r^2 = 0.706$), halocarbons vs. esters ($r^2 = 0.569$), halocarbons vs. alcohols ($r^2 = 0.569$), ethers vs. ketones ($r^2 = 0.602$), aldehydes vs. nitrogenated ($r^2 = 0.617$), ketones vs. esters ($r^2 = 0.542$, $p \leq 0.05$) and aromatic hydrocarbons vs. ethers ($r^2 = 0.538$, $p \leq 0.05$), suggesting a possible common source, generation and/or formation of these compounds. On the other hand, most aromatic hydrocarbons and aldehyde emission rates exhibited strong correlations with the rest of VOC of their family (Tables 8, 9). It has to be noted, that naphthalene and methyl-naphthalenes only correlate with themselves, and that benzene does not correlate with any other aromatic hydrocarbon, as it had been observed in previous studies (Kim and Kim, 2002; Kim et al., 2008). These facts indicate different sources for benzene, naphthalene and methyl-naphthalenes, and the rest of aromatic hydrocarbons. Regarding aldehyde correlations, only the heavier compounds correlated significantly with each other, i.e. heptanal, octanal, nonanal and decanal.

On the other hand, 1,1,1-trichloroethane and carbon tetrachloride were strongly correlated ($r^2 = 0.722$, F-Snedecor, $p \leq 0.001$),

Table 7

Percentage of the emission rate for each VOC in respect to the aggregated emission rate, and percentage of the emission rate for each VOC in respect to its familial aggregated emission rate ($n = 15$). Main contributors to the emission rates are shaded in gray.

Compound	% in respect to all VOC	% in respect to its family
Alkanes		
Cyclohexane	0.1 ± 0.1	1.4 ± 0.7
<i>n</i> -Decane	0.04 ± 0.05	0.5 ± 0.5
<i>n</i> -Hexane	0.4 ± 0.4	3.4 ± 1.8
<i>n</i> -Pentane	4.4 ± 5.3	38.5 ± 25.1
<i>n</i> -Tetradecane	4.1 ± 1.5	56.2 ± 26.9
Aromatic hydrocarbons		
1,2,3-Trimethylbenzene	0.04 ± 0.03	0.8 ± 0.3
1,2,4-Trimethylbenzene	0.2 ± 0.1	4.7 ± 1.6
1,3,5-Trimethylbenzene	0.04 ± 0.03	0.9 ± 0.3
1-Methylnaphthalene	0.03 ± 0.02	0.9 ± 0.6
2-Methylnaphthalene	0.07 ± 0.04	2.0 ± 1.3
Benzene	0.5 ± 0.4	9.6 ± 6.2
Ethylbenzene	0.2 ± 0.2	4.3 ± 2.0
<i>m+p</i> -Xylene	0.6 ± 0.5	13.4 ± 4.9
Naphthalene	0.07 ± 0.02	1.8 ± 0.9
<i>n</i> -Propylbenzene	0.01 ± 0.01	0.3 ± 0.2
<i>o</i> -Xylene	0.2 ± 0.2	4.2 ± 1.5
Styrene	0.1 ± 0.1	2.3 ± 1.8
Toluene	2.5 ± 1.1	54.8 ± 8.2
Alcohols		
1-Butanol	1.0 ± 0.4	13.5 ± 4.4
1-Propanol	0.1 ± 0.1	1.7 ± 1.0
Ethanol	2.2 ± 2.3	24.3 ± 15.1
Ethylhexanol	2.9 ± 1.1	38.8 ± 8.8
Isopropanol	0.2 ± 0.2	2.7 ± 3.1
Phenol	1.4 ± 1.1	19.1 ± 11.7
Ketones		
Acetone	9.2 ± 5.8	91.0 ± 5.1
Cyclohexanone	0.3 ± 0.1	4.2 ± 2.4
Methylethylketone	0.3 ± 0.4	3.0 ± 4.3
Methylisobutylketone	0.2 ± 0.1	1.8 ± 0.8
Halocarbons		
1,1,1-Trichloroethane	0.02 ± 0.01	1.2 ± 0.6
1,2-Dichloroethane	0.1 ± 0.1	5.7 ± 4.5
Carbon tetrachloride	0.4 ± 0.1	24.9 ± 14.2
Chlorobenzene	0.01 ± 0.02	0.6 ± 0.7
Chloroform	0.4 ± 0.2	19.7 ± 14.4
Dichloromethane	0.2 ± 0.2	12.4 ± 8.9
<i>o</i> -Dichlorobenzene	0.003 ± 0.003	0.3 ± 0.4
<i>p</i> -Dichlorobenzene	0.004 ± 0.002	0.3 ± 0.2
Tetrachloroethylene	1.0 ± 1.0	32.1 ± 22.7
<i>trans</i> -1,2-Dichloroethylene	0.01 ± 0.01	0.2 ± 0.4
Trichloroethylene	0.05 ± 0.03	2.6 ± 1.6
Aldehydes		
Benzaldehyde	0.1 ± 0.1	0.2 ± 0.2
Decanal	18.7 ± 6.1	40.9 ± 4.3
Heptanal	0.5 ± 0.2	1.2 ± 0.3
Hexanal	0.6 ± 0.3	1.5 ± 0.8
Nonanal	22.2 ± 7.5	48.9 ± 4.0
Octanal	3.2 ± 0.7	7.3 ± 1.4
Esters		
Butyl acetate	0.2 ± 0.1	20.0 ± 10.2
Ethyl acetate	0.6 ± 0.4	65.0 ± 12.8
Methyl acetate	0.1 ± 0.1	14.9 ± 5.3
Terpenoids		
α -Pinene	0.2 ± 0.1	38.6 ± 15.3
β -Pinene	0.1 ± 0.1	23.6 ± 11.1
D-Limonene	0.2 ± 0.2	28.5 ± 21.1
<i>p</i> -Cymene	0.05 ± 0.04	9.4 ± 7.0
Ethers		
<i>tert</i> -Butyl ethyl ether	0.8 ± 0.8	92.2 ± 8.9
<i>tert</i> -Butyl methyl ether	0.1 ± 0.1	7.8 ± 8.9
Nitrogenated compounds		
Acetonitrile	0.003 ± 0.0007	0.2 ± 0.7
Cyclohexane isocyanato	0.1 ± 0.1	96.5 ± 1.9
Cyclohexane isothiocyanato	0.002 ± 0.001	3.2 ± 1.9
Sulfur compounds		
Carbon disulfide	0.2 ± 0.3	–
Furans		
Tetrahydrofuran	0.1 ± 0.2	–
Carboxylic acids		
Acetic acid	18.7 ± 7.5	–

indicating in this case a single source for this pair of compounds. 1,1,1-Trichloroethane and carbon tetrachloride uses and properties are similar, they have been mainly employed as solvents, cleaning and degreasing agents, refrigeration fluids and propellants. It has to be taken into account that 1,1,1-trichloroethane replaced carbon tetrachloride in many of its uses around 1960 due to its less toxic character (Doherty, 2000). Their vapor pressures (at 20 °C) and boiling points are also highly similar, being 100 mm Hg and 74.1 °C, and 91.3 mm Hg and 76.7 °C for 1,1,1-trichloroethane and carbon tetrachloride, respectively. The observed higher concentrations of carbon tetrachloride in respect to 1,1,1-trichloroethane could be explained by a higher volume of buried waste containing this chlorinated compound, as several studies have pointed out that carbon tetrachloride degradation and/or dechlorination is generally faster than that of 1,1,1-trichloroethane (Doong and Wu, 1996; Choi et al., 2009).

3.1.3. BTEX ratios

Each landfill presents its concrete and unique emission pattern, mainly due to particular characteristics such as type of buried waste, operational conditions, time passed since its closing, base soil and cover types, topography and climatology. However, benzene, toluene, ethylbenzene and xylene (BTEX) ratios have been generally used to establish possible emission sources (Zou et al., 2003; Wang and Zhao, 2008; Durmusoglu et al., 2010). In the present study, surface emission BTEX average ratio with ethylbenzene based normalization was 4:18:1:5. In other studies evaluating landfill emissions, the BTEX ratio has been found highly variable, e.g. 0:1:1:4 or 7:44:1:23 (Scheutz et al., 2003, 2008; Barlaz et al., 2004). Additionally, in landfill atmospheric environments this ratio presents values of 1:5:1:1 (Durmugoglu et al., 2010); 4:6:1:2 and 3:5:1:2 (Zou et al., 2003); and 1:8:1:3 and 2:9:1:2 (Kim and Kim, 2002).

Benzene to toluene (B:T) ratio could be a better variable to evaluate emission sources. B:T in the collected samples range from 0.1 to 0.4, with an average value of 0.2 ± 0.1 . In landfill gas and in landfill surrounding atmospheres, this ratio is usually found around 0.1–0.2 (Kim and Kim, 2002; Kim et al., 2008; Tassi et al., 2009; Durmusoglu et al., 2010), whereas other sources such as traffic present B:T values generally >0.5, ranging from 0.3 to 2.0 (Simon et al., 2004; Han and Naeher, 2006; Schnitzhofer et al., 2008; Wang and Zhao, 2008; Wang et al., 2013), highly depending on fuel composition. The B:T ratio obtained from the emission rates of the studied landfill is related to the different sources of benzene and the rest of aromatic hydrocarbons in the disposed waste, as it has been explained in the previous section. This suggests that the factors that regulate aromatic hydrocarbon distributions in the landfill emissions are different from those typical found in urban areas, where benzene emissions are more related to motor vehicle exhausts (Kim and Kim, 2002; Lan and Binh, 2012). The B:T ratios found could be linked to buried waste types such as asphalts, degreasing agents, paints and dry cleaning products (Vega et al., 2000).

3.2. Influence of environmental conditions

Ambient atmospheric pressure fluctuations and wind interaction with the terrain have been observed to cause gas movement through the unsaturated porous medium of the soil surface, causing pressure pumping and the possibility to generate considerable heterogeneities in the pollutant emission fluxes determined in different soil surfaces (Czepiel et al., 2003; Takle et al., 2004; Rochette, 2011). The rate of change in atmospheric pressure and landfill gas emissions has been inversely correlated in several studies, expecting higher emissions when the atmospheric pressure decreases (Gebert and Groengroeft, 2006; Einola et al., 2009). In the present study, atmospheric pressure variations were small, ranging from 1008 to 1018 hPa, with an average value of 1013 ± 3 hPa. There was neither a significant correlation between the obtained VOC emission rates and the atmospheric

Table 8

Correlation coefficients (r^2) of the emission rates of the different aromatic hydrocarbons studied ($n = 15$). Bold values correspond to significant correlations (F-Snedecor, $p < 0.001$).

Aromatic hydrocarbons	1,2,4-TMB	1,3,5-TMB	1-MNPT	2-MNPT	Benzene	Ethylbenzene	<i>m</i> + <i>p</i> -Xylene	Naphthalene	<i>n</i> -Propylbenzene	<i>o</i> -Xylene	Styrene	Toluene
1,2,3-TMB ^a	0.954	0.856	0.206	0.247	0.056	0.924	0.859	0.590	0.825	0.838	0.966	0.783
1,2,4-TMB		0.924	0.203	0.203	0.092	0.950	0.942	0.522	0.848	0.929	0.939	0.809
1,3,5-TMB			0.247	0.225	0.142	0.893	0.916	0.466	0.879	0.904	0.851	0.869
1-MNPT ^b				0.810	0.004	0.245	0.193	0.586	0.171	0.176	0.164	0.216
2-MNPT					0.007	0.267	0.162	0.814	0.198	0.140	0.209	0.285
Benzene						0.121	0.184	0.033	0.145	0.212	0.030	0.341
Ethylbenzene							0.959	0.562	0.864	0.939	0.928	0.864
<i>m</i> + <i>p</i> -Xylene								0.413	0.840	0.997	0.851	0.845
Naphthalene									0.443	0.381	0.525	0.544
<i>n</i> -Propylbenzene										0.824	0.825	0.882
<i>o</i> -Xylene											0.826	0.838
Styrene												0.748

^a Trimethylbenzene.

^b Methyl-naphthalene.

pressure nor between the emission rates and atmospheric pressure changes.

On the other hand, underestimation of emissions due to chemical reactions and physical phenomenon has been observed when high values of relative humidity (>90%) have been tested, mainly as a cause of water condensation and water film formation on the sampling device (Kolari et al., 2012). Relative humidity recorded during the sampling campaign ranged from 37 to 68%, with an average value of $56 \pm 9\%$. As in the previous case, no significant correlations were found between VOC emission rates and relative humidity.

Additionally, several studies have perceived an increase in pollutant emissions when temperature increases inside the sampling chamber, in the atmospheric surrounding of the landfill and/or in the soil surface (Park and Shin, 2001; Zou et al., 2003; Durmusoglu et al., 2010; Kolari et al., 2012). In the present study, aldehyde emissions were significantly correlated (F-Snedecor, $p < 0.001$) with temperature. Due to the great familial contribution of these compounds to the total emission rate (45%), total emission rate also correlated significantly (F-Snedecor, $p < 0.001$) with temperature. Nonetheless, the rest of VOC emission rates did not correlate with temperature.

3.3. Calculation of average TVOC emissions from the landfill

The average TVOC emission from the studied landfill per unit of time can be calculated using the three procedures presented in Section 3.1. Total VOC emissions were 237 ± 48 , 222 ± 46 and 77 ± 17 g day⁻¹ for *Global*, *Tributary area* and *Kriging* procedures, respectively. The spatial distributions of TVOC emissions in the studied landfill for the three data processing methodologies, *Global*, *Kriging*, and *Tributary area*, are presented in Fig. 4. The *Global* figure shows the averaged global emission TVOC value, which has been obtained averaging all the experimental TVOC emission values for each one of the five sampling points. The

Kriging figure shows the triangle-linear interpolated values using the average values for each one of the five sampling points, and with zero values at the outside of the emission area considered. The *Tributary area* figure presented has been also obtained using the average values at the five sampling points. These last two figures are presented only to visualize the different methods used, as all the possible combinations of the data obtained at each individual sampling point were used in the statistical calculation. As it should be expected, the total emission from the lastly filled bucket (South) (years 1988–1995) is higher than the one from the older section in the landfill (North and North-East buckets, years 1982–1988), as can be seen in *Kriging* and *Tributary area* graphics plotted in Fig. 4.

4. Conclusions

The evaluation of atmospheric emissions of a wide range of VOC from a closed industrial landfill has corroborated the good performance of the presented self-designed flux chamber. VOC sampling using multi-sorbent tubes and analysis through TD-GC/MS is a very versatile method for the analysis of these compounds at very low levels, being satisfactory sensitive, selective and reproducible. At the same time, surface emission rates of sixty VOC have been determined for a closed industrial landfill, generating a valuable database that can be useful in future studies related to industrial landfill management. The analysis of the results through *Global* and *Tributary area* methodologies presented considerably similar values, with total VOC emissions of 237 ± 48 and 222 ± 46 g day⁻¹, respectively; however, *Kriging* obtained values were lower, 77 ± 17 g day⁻¹. The total emission from the lastly filled bucket is higher than the emission from the older section in the landfill, as it could be expected.

Conflict of interest

The authors have no current or potential conflicts of interest to declare.

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Table 9

Correlation coefficients (r^2) of the emission rates of the different aldehydes ($n = 15$). Bold values correspond to significant correlations (F-Snedecor, $p < 0.001$).

Aldehydes	Decanal	Heptanal	Hexanal	Nonanal	Octanal
Benzaldehyde	0.459	0.396	0.228	0.313	0.377
Decanal		0.845	0.260	0.901	0.779
Heptanal			0.512	0.812	0.777
Hexanal				0.145	0.232
Nonanal					0.822

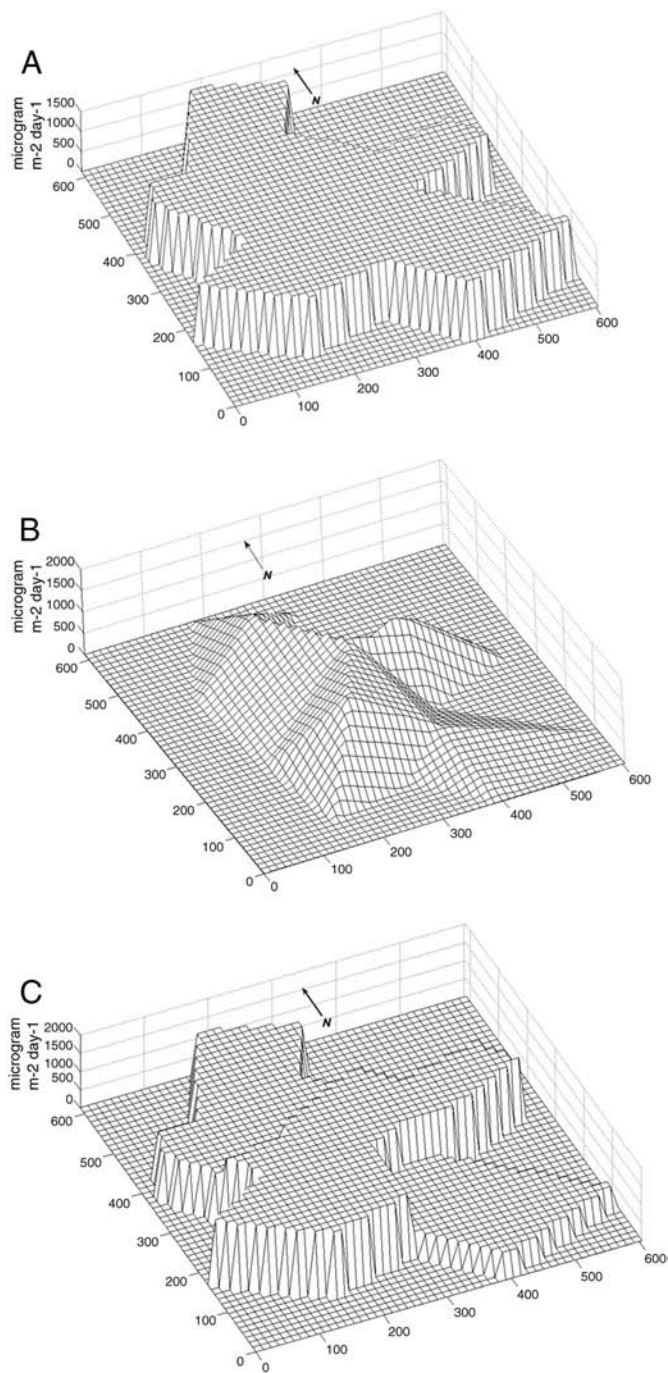


Fig. 4. Spatial distribution of TVOC emissions in the studied landfill. A) Global, B) Kriging, C) Tributary area.

References

- Barlaz MA, Green RB, Chanton JP, Goldsmith CD, Hater GR. Evaluation of a biologically active cover for mitigation of landfill gas emissions. *Environ Sci Technol* 2004;38:4891–9.
- Bernstein JA, Alexis N, Bacchus H, Bernstein IL, Fritz P, Horner E, et al. The health effects of nonindustrial indoor air pollution. *J Allergy Clin Immunol* 2008;121:585–91.
- Carazo Fernández L, Fernández Álvarez R, González-Barcala FJ, Rodríguez Portal JA. Indoor air contaminants and their impact on respiratory pathologies. *Arch Bronconeumol* 2013;49:22–7.
- Chemel C, Riesenmey C, Batton-Hubert M, Vaillant H. Odour-impact assessment around a landfill site from weather-type classification, complaint inventory and numerical simulation. *J Environ Manage* 2012;93:85–94.
- Chiriac R, De Araujos Morais J, Carre J, Bayatd R, Chovelon JM, Gourdon R. Study of the VOC emissions from a municipal solid waste storage pilot-scale cell: comparison with biogases from municipal waste landfill site. *Waste Manag* 2011;31:2294–301.
- Choi J, Choi K, Lee W. Effects of transition metal and sulfide on the reductive dechlorination of carbon tetrachloride and 1,1,1-trichloroethane by FeS. *J Hazard Mater* 2009;162:1151–8.
- Christiansen JR, Korhonen JFJ, Juszczyk R, Giebels M, Pihlatie M. Assessing the effects of chamber placement, manual sampling and headspace mixing on CH₄ fluxes in a laboratory experiment. *Plant Soil* 2011;343:171–85.
- CTM (Centre Tecnològic de Manresa). Memoria del estudio de impacto ambiental del vertedero de residuos industriales y residuos sólidos urbanos emplazados en Can Planas (Cerdanyola del Vallès). Informe Final; 2003.
- Czepiel PM, Shorter JH, Mosher B, Allwine E, McManus JB, Harriss RC, et al. The influence of atmospheric pressure on landfill methane emissions. *Waste Manag* 2003;23:593–8.
- Doherty RE. A history of the production and use of carbon tetrachloride, tetrachloroethylene, trichloroethylene and 1,1,1-trichloroethane in the United States: Part 2-Trichloroethylene and 1,1,1-trichloroethane. *Environ Forensics* 2000;1:83–93.
- Doong R-A, Wu S-C. Effect of substrate concentration on the biotransformation of carbon tetrachloride and 1,1,1-trichloroethane under anaerobic conditions. *Water Res* 1996;30:577–86.
- Durmusoglu E, Taspinar F, Karademir A. Health risk assessment of BTEX emissions in the landfill environment. *J Hazard Mater* 2010;176:870–7.
- Einola J, Sormunen K, Lensu A, Leiskallio A, Ettala M, Rintala J. Methane oxidation at a surface-sealed boreal landfill. *Waste Manag* 2009;29:2105–20.
- El-Fadel M, Abi-Esber L, Salhab S. Emission assessment at the Burh Hammoud inactive municipal landfill: viability of landfill gas recovery under the clean development mechanism. *Waste Manag* 2012;32:2106–14.
- Fourie AB, Morris JW. Measured gas emissions from four landfills in South Africa and some implications for landfill design and methane recovery in semi-arid climates. *Waste Manag Res* 2004;22:440–53.
- Gallego E, Roca FJ, Perales JF, Guardino X. Simultaneous evaluation of odor episodes and air quality. Methodology to identify air pollutants and their origin combining chemical analysis (TD-GC/MS), social participation, and mathematical simulation techniques. In: Romano GC, Conti AG, editors. *Air quality in the XXI Century*. New York: Nova Science Publishers; 2009. p. 139–209.
- Gallego E, Roca FJ, Perales JF, Guardino X. Odor control in urban areas originated from multiple focuses. Identification of potentially toxic compounds. In: Daniels JA, editor. *Advances in Environmental Research*, vol. 14. New York: Nova Editors; 2011. p. 261–88.
- Gao F, Yates SR. Laboratory study of closed and dynamic flux chambers: experimental results and implications for field application. *J Geophys Res* 1998;103:26115–25.
- Gebert J, Groengroeft A. Passive landfill gas emission – influence of atmospheric pressure and implications for the operation of methane-oxidising biofilters. *Waste Manag* 2006;26:245–51.
- Han X, Naeher LP. A review of traffic-related air pollution exposure assessment studies in the developing world. *Environ Int* 2006;32:106–20.
- Hudson N, Ayoko GA. Odour sampling. 2. Comparison of physical and aerodynamic characteristics of sampling devices: a review. *Bioresour Technol* 2008;99:3993–4007.
- IDOM. Estudi de delimitació i activitat de l'abocador de Can Planas. Anàlisi de solucions. Definició de la solució adoptada a nivell d'avantprojecte. Fase II. Treballs d'investigació i diagnòstic mediambiental; 2008a.
- IDOM. Estudi de delimitació i activitat de l'abocador de Can Planas. Anàlisi de solucions. Definició de la solució adoptada a nivell d'avantprojecte. Fase I. Diagnòstic preliminar i proposta d'investigació; 2008b.
- Kim K-H, Kim M-Y. The distribution of BTEX compounds in the ambient atmosphere of the Nan-Ji-Do abandoned landfill site in Seoul. *Atmos Environ* 2002;36:2433–46.
- Kim K-H, Shon Z-H, Kim M-Y, Sunwoo Y, Jeon E-C, Hong J-H. Major aromatic VOC in the ambient air in the proximity of an urban landfill facility. *J Hazard Mater* 2008;150:754–64.
- Kolari P, Bäck J, Taipale R, Ruuskanen TM, Kajos MK, Rinne J, et al. Evaluation of accuracy in measurements of VOC emissions with dynamic chamber system. *Atmos Environ* 2012;62:344–51.
- Lan TTN, Binh NTT. Daily roadside BTEX concentrations in East Asia measured by the Lanwatsu, Radiello and Ultra I SKS passive samplers. *Sci Total Environ* 2012;441:248–457.
- Lee GF, Jones-Lee A. Impact of municipal and industrial non-hazardous waste landfills on public health and the environment: an overview. California EPA Comparative Risk Project. Sacramento (CA); 1994.
- Lindberg SE, Zhang H, Vette AF, Gustin MS, Barnett MO, Kuiken T. Dynamic flux chamber measurement of gaseous mercury emission fluxes over soils: part 2—effect of flushing flow rate and verification of a two-resistance exchange interface simulation model. *Atmos Environ* 2002;36:847–59.
- Liu G, Si BC. Multi-layer diffusion model and error analysis applied to chamber-based gas fluxes measurements. *Agr Forest Meteorol* 2009;149:169–78.
- Milner J, Vardoulakis S, Chalabi Z, Wilkinson P. Modelling inhalation exposure to combustion-related air pollutants in residential buildings: application to health impact assessment. *Environ Int* 2011;37:268–79.
- Park J-W, Shin H-C. Surface emission of landfill gas from solid waste landfill. *Atmos Environ* 2001;35:3445–51.
- Parker D, Ham J, Woodbury B, Cai L, Spiels M, Rhoades M, et al. Standardization of flux chamber and wind tunnel flux measurements for quantifying volatile organic compound and ammonia emissions from area sources at animal feeding operations. *Atmos Environ* 2013;66:72–83.
- Parker DB, Gilley J, Woodbury B, Kim K-H, Galvin G, Bartelt-Hunt SL, et al. Odorous VOC emissions following land application of swine manure slurry. *Atmos Environ* 2013;66:91–100.
- Pedersen AR, Petersen SO, Schelde K. A comprehensive approach to soil-atmosphere trace-gas flux estimation with static chambers. *Eur J Soil Sci* 2010;61:888–902.

- Pihlatie MK, Christiansen JR, Aaltonen H, Korhonen JFJ, Nordbo A, Tasilo T, et al. Comparison of static chambers to measure CH₄ emissions from soils. *Agr Forest Meteorol* 2013;171–172:124–36.
- Ribes A, Carrera G, Gallego E, Roca X, Berenguer MJ, Guardino X. Development and validation of a method for air-quality and nuisance odors monitoring of volatile organic compounds using multi-sorbent adsorption and gas chromatography/mass spectrometry thermal desorption system. *J Chromatogr A* 2007;1140:44–55.
- Rochette P. Towards a standard non-steady-state chamber methodology for measuring soil N₂O emissions. *Anim Feed Sci Technol* 2011;166–167:141–6.
- Scheutz C, Bogner J, Chanton J, Morcet M, Kjeldsen P. Comparative oxidation and net emissions of methane and selected non-methane organic compounds in landfill cover soils. *Environ Sci Technol* 2003;37:5150–8.
- Scheutz C, Bogner J, Cjanton JP, Blake D, Morcet M, Aran C, et al. Atmospheric emissions and attenuation of non-methane organic compounds in cover soils at a French landfill. *Waste Manag* 2008;28:1892–908.
- Schnitzhofer R, Beauchamp J, Dunkl J, Wisthaler A, Weber A, Hansel A. Long-term measurements of CO, NO, NO₂, benzene, toluene and PM₁₀ at a motorway location in an Australian valley. *Atmos Environ* 2008;42:1012–24.
- Simon V, Baer M, Torres L, Olivier S, Meybeck M, Della Massa JP. The impact of reduction in the benzene limit value in gasoline on airborne benzene, toluene and xylenes levels. *Sci Total Environ* 2004;334–335:177–83.
- Take ES, Massman WJ, Brandle JR, Schmidt RA, Zhou X, Litvina IV, et al. Influence of high-frequency ambient pressure pumping on carbon dioxide efflux from soil. *Agr Forest Meteorol* 2004;124:193–206.
- Tassi F, Montegrossi G, Vaselli O, Liccioli C, Moretti S, Nisi B. Degradation of C₂–C₅ volatile organic compounds in a landfill cover soil. *Sci Total Environ* 2009;407:4513–25.
- US EPA. Compendium of methods for the determination of toxic organic compounds in ambient air. Method TO-15, EPA/625/R-96/010b. Cincinnati: Center for Environmental Research Information, Office of Research and Development; 1999.
- Vega E, Mugica V, Carmona R, Valencia E. Hydrocarbon source apportionment in Mexico City using the chemical mass balance receptor model. *Atmos Environ* 2000;34:4121–9.
- Wang P, Zhao W. Assessment of ambient volatile organic compounds (VOCs) near major roads in urban Nanjing, China. *Atmos Res* 2008;89:289–97.
- Wang J, Jin L, Gao J, Shi J, Zhao Y, Liu S, et al. Investigation of speciated VOC in gasoline vehicular exhaust under ECE and EUDC test cycles. *Sci Total Environ* 2013;445–446:110–6.
- Zou SC, Lee SC, Chan CY, Ho KF, Wang XM, Chan LY, et al. Characterization of ambient volatile organic compounds at a landfill site in Guangzhou, South China. *Chemosphere* 2003;51:1015–22.