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Characterisation of VOCs emitted by open cells receiving municipal solid waste

Review

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Abstract

This study gives relevant information on the variation of concentrations of certain volatile organic compounds (BTEX, alkanes, organochlorides and terpenes) emitted by open cells receiving municipal solid waste. These compounds represent a large fraction of the total trace components present in landfill gas.

The VOC measurements were carried out in the atmosphere of an open landfill cell as a function of time and meteorological parameters, but also as a function of the activity of trucks unloading waste and compaction vehicles, in order to identify the factors that influence VOC emissions. Comparisons were performed systematically between the surface of the open cell and the corresponding mechanical activity. The measurements carried out during the course of the day highlighted the influence of air temperature and waste composition on VOC emissions while measurements of activity showed that the activity of fresh waste compaction vehicles is responsible for the highest VOC emissions. Such information is essential since most of the data in the literature relate to analyses of VOC traces in the biogas network and not in the air of the open cells as a function of different parameters (i.e. meteorological parameters, activity on the site). The highest VOC concentrations (in $\mu g/m^3$) in the area of an open cell were obtained for: tetrachloroethylene (9810), toluene (8230), limonene (4550), *m*-xylene (3980) and trichloroethylene (3680).

The results showed that the TWA values (the time-weighted average concentrations for up to an 8-h workday) established by INRS/France for the personnel in the station were complied with on the site studied.

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Keywords: Volatile organic compounds; Municipal solid waste; Landfill gas; Sorbent tubes; Trace component

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1. Introduction

Burial of municipal solid waste in landfills without pretreatment is one of the two main methods used to eliminate waste in France and will be for at least one or two decades.

In 2002, according to ADEME (Environment and Energy Management Agency), about 40% of MSW was landfilled versus 12% for recycling and 42% for incineration.

Landfill gas is produced continuously by microbial action on biodegradable wastes under anaerobic conditions. Methane and carbon dioxide are the major constituents of landfill gas and greatly contribute to the greenhouse effect [1-4]. Small amounts of other gases (non-methane volatile organic compounds) are also present in landfill gas. These trace components can be formed either from intermediate biochemical reactions associated with degradation processes, or by degradation and volatilisation of other organic materials deposited in the landfill. In all, these trace components may make up less than 1-2%of the gas emitted from the waste in a landfill [2,5]. However, the impact of certain trace gases on the environment and potentially on human health may be more significant than that of the bulk gases (e.g. CH₄ and CO₂). Over 500 compounds have been reported in landfill gas [6]. These VOC emissions include higher amounts of alkanes and alkenes, cycloalkanes and cycloalkenes, aromatic, cyclic aromatic and polycyclic aromatic hydrocarbons and derivatives, aldehydes, alcohols, ketones, esters, organohalogens and organosulphur compounds.

The main sources of these VOC emissions are: (i) faults in capping or gas collection; (ii) open leacheate chambers; (iii) faults (cracks) in the liners and covers of closed cells; (iv) open cells.

The sources of faults and cracks can only be remedied by mechanical treatment; on the contrary, VOC emissions caused by open cells are much more difficult to estimate and reduce.

Open cells are cells that receive waste arriving in a landfill and from which certain VOCs are emitted into the ambient air. Although the waste is covered by soil (e.g. clay), which helps to limit VOC diffusion, a small amount of these VOCs continues to diffuse into the ambient air. Therefore the purpose of this study was to set up a technical analytical procedure for measuring VOC emissions produced by open cells. A bibliographical study was initially carried out to guide our choice. The results of this study are presented in Table 1.

The study of these articles showed that most measurements were carried out on the landfill gas collection systems (e.g. the main line carrying gas to the engines or site flare, gas field manifolds, individual gas wells) [2,3,9,11,12,14,15,17,18,21,22]. Some of them [5,8,16] were performed in the ambient air of the site or in the vicinity of the site, without however being positioned to evaluate the level of emission as a function of the activity of the vehicles (unloading, spreading and compaction of waste) and meteorological parameters.

Only Davoli et al. [7] have carried out several measurement campaigns of air samples from the most significant emission sources of the landfill: (i) emissions from fresh wastes (characterised by limonene); (ii) emissions from older wastes (buried before biogas collection) as well as biogas and leachate, characterised by *p*-cymene; (iii) emissions at the entrance of the landfill; (iv) emissions collected at further distances (1.5, 3 and 6 km).

Another publication [23] asserts that the strongest waste odours (VOCs) are generated during discharge and compaction of waste (though gives no references or experimental results). These authors assert that disturbing waste creates new surfaces and exposes old surfaces from which volatiles can evaporate. The action of depositing more waste at each site simply results in generating more odours. However, once the waste has been compacted and covered, the rate of odour generation appears to decline rapidly. Compaction reduces the active surface available for odour generation while covering reduces the rate of volatilisation as vapour pressures develop between the waste surface and the covering layer. On the other hand, this work did not take into account the influence of ambient climatic conditions.

The study presented here comes from an ADEME thesis [24] whose objective was to investigate the emission and dispersion phenomena of certain VOCs emitted by a landfill site. It is essential to know the influence of the parameters acting on the emission of VOCs before studying their dispersion in the atmosphere.

Initially, the measurements were limited to the following chemical families: aromatics (BTEX and trimethylbenzene), organohalogens, alkanes and terpenes. These compounds are an important fraction of the total trace components present in landfill gas [6] and some of them are toxic compounds. This choice was confirmed afterwards in another study [9] based on the VOC compounds present in fresh waste. For technical reasons (i.e. poor sorption on activated carbon, etc.), the study of high volatile compounds (e.g. vinyl chloride) was excluded from the study.

2. Materials and methods

2.1. Sampling procedure

Table 1 shows three analytical procedures: (i) sampling in canisters (or bags) without preconcentration of gas samples and

Table 1 Sampling and analytical procedures for VOCs emitted by municipal solid waste landfills

Article reference	Sampling method	Analytical method
[2,9]	Adsorption on tubes (500 mL of landfill gas at 50 mL/min)—combination of 3 adsorbents (Tenax TA, Chromosorb 102 and Carbosieve S-III)	Perkin-Elmer ATD 50/Hewlett Packard GC 5890/Hewlett Packard MS 5970
[3]	Sampling in canisters and laboratory analysis	GC equipped with dual columns and multiple detectors (FID, PID, ELCD)
[5]	Adsorption (40 min at 0,25 L/min) on Carbontrap-300 (Tekmar, USA) consisting of Tenax, Carbonsieve S-III and silica gel	Tekmar 6032 Aerotrap/Tekmar 3000 Purge and Trap Concentrator/Hewlett Packard GC 5890/Hewlett Packard MS 5972
[7]	 Sampling in Nalophan bags (9 L) and concentration in laboratory by SPME: 3 types of fibers (Supelco, USA) were used: PDMS 100 μm; PDMS/Carboxen 85 μm; DVB/Carboxen/PDMS 50–30 μm On-site sampling with a pre-concentrator-thermo-desorber, μTD (SRA CONVOY, Italy) coupled with a μGC 	 Desorption from the fiber for 3 min in the GC injection port and analysis by Varian 3800 GC/Varian Saturn 2000 MS On-site analysis with μGC Agilent P200 (with PLOT Q and OV1 capillary columns and thermal conductivity detector)
[8,10]	Sampling in Tedlar bag of 3 or 10 L	Peltier cooling/Thermal desorption system combined with GC/FID
[11]	 Adsorption on tubes (10–20 min at 0,6 L/min): Carbotrap-300 from Supelco (with 425 mg Carbotrap C, 500 mg Carbotrap B and 350 mg Carbosieve S-III); Tenax GC from Supelco 	Thermal desorption (Tekmar LSC-2000/Perkin-Elmer 8500 GC/MS)
[12]	Adsorption on tubes ATD—combination of 3 adsorbents (Tenax GR, Haysep Q et Carbosieve S-III)	Perkin-Elmer ATD 50/Hewlett Packard GC 5890/Hewlett Packard MS 5970
[13]	Sampling in Nalophan bags (9 L) and concentration by SPME: PDMS/Carboxen/DVB/65-µm fiber (Supelco, USA)	Hewlett Packard GC 5890/Hewlett Packard MS 5971
[14]	Adsorption on tubes (at 50 mL/min)—combination of adsorbents (Tenax TA and Carbosieve S-III)	Perkin-Elmer ATD 400/Perkin-Elmer GC 8320 with FID/Perkin-Elmer Ion Trap detector
[15]	Sampling in 15 L stainless steel canisters (Tekmar)	Hewlett Packard GC 5890/Hewlett Packard MS 5971 A/Hewlett Packard 5921 A AED
[16]	Adsorption on tubes (50 mL/min)—combination of 3 adsorbents: Carbotrap C (C4–C14), Carbotrap B (C4–C14) and Carbosieve S-III (low-weight VOCs with C2–C6)	Perkin-Elmer ATD 400/GC/FID
[17]	• ATD tubes coated with silicosteel or sulphinert—combination of 2 adsorbents: Tenax for less volatile compounds and Unicarb for more volatile analytes (vinyl chloride, methanethiol): Sampling volume: 0.5–2 L:	• ATD/GC/MS;
	 DNPH impregnated silica gel tubes; Silica gel sorbents 	 HPLC with UV detection; Desorption with a water/formic acid mixture and GC/FID (with polyethylene glycol phase column).
[18]	Activated carbon traps;Sampling in inert Nafion bags and concentration with SPME	Méthanol extraction and GC/MS;GC/MS
[19]	Adsorption (5 L at 200 mL/min) on three layer sorbent glass tubes containing 300 mg Carbopack C, 200 mg Carbopack B and 125 mg Carbosieve S-III, from Supelco, USA	"In-house-made" thermal desorption unit/Hewlett Packard GC 5890/Hewlett Packard MS 5972
[20]	Sampling in Teflon-Tedlar bags of 5 L with SKC vacuum pumps of 500 mL/min	Analyse HP 6890 GC/FID with purge and trap system for introduction of VOC into the GC
[21]	Adsorption on Tenax	Thermal desorption/gas-chromatography

laboratory analyses; (ii) sampling on sorbent tubes (or fibers) followed by laboratory analyses; (iii) on-site analysis with portable material.

Previous works [25,26], realised in our laboratory, pointed out that sampling polluted air requires fast analysis, which is incompatible with measurements over a half-day or a whole day. Analyses with portable material under difficult conditions (e.g. measurements on compaction vehicles) are obviously also difficult to carry out. Thus all the sampling procedures were performed by concentration on sorbent tubes. Taking into account the compounds to be analysed, sampling on activated carbon was chosen for the following reasons: (i) sampling on activated carbon corresponds to standards NF X 43-252 (1991) [27] and NF ISO 16200-1 (2001) [28], the second being used during the works; (ii) the sorbent tubes were preserved without deterioration in the refrigerator; (iii) the samples were taken in the atmosphere, thus the gas mixture trapped on the tube was never saturated with water, allowing the use of activated carbon for quantitative analysis.

Date	Humi	dity ^a (%)		Temper	ature ^a (°C	C)	Wind	d speed ^a (m/s)	Atmosph	neric pressu	re ^a (HPa)	
7 April	15	34	48	4.4	5.8	7.5	4	5.7	7	949.3	949.7	950.1	
30 April	30	62.3	95	2.7	10.1	18.5	1	1.2	2	949.5	951.0	952.1	
23 May	20	39.8	81	11.9	26	34	0	2	4	947.8	950	956.3	
12 June	39	42.8	46	23.9	26.3	27	1	1.7	3	953.7	955.1	954.3	
23 July	47	53.2	61	24.7	26	27.1	0	1.9	3	956.1	956.5	956.9	

Table 2Meteorological parameters for all measurements

^a Minimal, average and maximal values.

All the samples were taken using SKC activated carbon tubes (Arelco, France, #226-01). These tubes are composed of two parts: the second permitted checking the breakthrough phenomena of the first part used for quantitative analysis. Only a small quantity of activated carbon was used, thus well adapted to VOC trace analysis and allowing the use of a small quantity of solvent $(1 \text{ cm}^3 \text{ for the first part and } 0.5 \text{ cm}^3 \text{ for the second part})$. When the second part of the sorbent tube showed a concentration value of more than 5% for a VOC compound compared to that obtained in the first part, we considered that the breakthrough volume had been reached and did not take this concentration value into account. However when the concentration found in the second part of the tube was lower than 5% compared to that found in the first part, the two concentrations were added together.

Concerning the sampling procedure, several pumps with different flow rates were used. The choice of sampling flow rate is presented in Section 3.1.

The sampling location was selected as close as possible (between 1 and 10 m according to possibilities of access) to the source (i.e. at the edge of the open cell, in the area of the trucks tipping waste, on compaction vehicles) and was positioned according to the direction of the wind bearing the VOCs. The meteorological parameters for all measurements were obtained from the meteorological station present on site (Table 2). The sampling parameters for each day of measurement (rate, time) are given in Table 3. This table also provides the distance between the sampling location and the upper layer of waste, as well as the area of the open cell and the surface density of the waste (volume of waste per day/cell surface area), since, given the VOC dispersion the surface density represents the waste deposited near the sample more accurately (the waste deposited at the other end of the cell is not involved). All the samples were taken at the same location on each day of the measurement campaign.

On May 23 samples were taken every hour, above the open cell (in the morning at a height of 3–4 m from the waste surface and in the evening at less than 1 m, due to the waste filling only one part of the cell during the day). The temperatures were cool in the morning, ranging from 10 to $15 \,^{\circ}$ C; they reached $27 \,^{\circ}$ C at midday and increased up to $33–34 \,^{\circ}$ C at the beginning of the afternoon. They finally reached $28 \,^{\circ}$ C at the end of the measurements. It should be noted that these temperatures measured at the sampling location with an anemometer (CONTROLAB, France, #D3040.1) were in perfect agreement with those obtained from the meteorological station.

All the samples were taken under stable meteorological conditions, meaning that the pressure and the wind speed varied little during the sampling period. Thus the variations were insufficient to affect the concentrations emitted during each measurement period. The direction of the wind did not have any effect either as the measurements were performed at a constant wind direction. This is the reason why certain measurements could only be performed for half-day periods due to varying wind direction (for example, the afternoon of April 7), thus it was not possible to take reliable samples without changing the sampling location.

For the measurements performed on July 23, one of the sampling pumps was located at the edge of the cell in operation at a distance of 1 m from the superior layer of waste, whereas the other pump was installed on the compaction vehicle, near (and outside) the driver's cab and far from the exhaust pipe so that the exhaust emission did not interfere with the emissions from the waste.

The VOC emissions generated at the cell in operation included both VOCs from the waste and those contained in the exhaust gas of the compaction vehicles and trucks operating at

Table 3	
Sampling parameters for all measurements	

Date	Area of the open cell (m ²)	Height ^a (m)	Sampling rate (L/min)	Sampling time/tube (min)	Surface density of waste $m^3/(m^2 \cdot day)$
12 June	3100	8-10	0.75	60	0.30
30 April	5700	5	0.75	60	0.31
7 April	3330	2–3	0.63	15	0.33
23 May	7140	1	0.63/0.75 ^b	60	0.27
23 July	_d	0	0.63/0.75°	60/50	_d

^a Distance between the superior layer of waste and the sampling location.

^b 0.63 for sampling on open cell and 0.75 for sampling on truck area.

^c 0.63 for sampling on open cell and 0.75 for sampling on compaction vehicle.

^d No data available.

this location, since all the emissions were taken into account in the study of the dispersion of VOCs emitted (forthcoming publication). However, in an attempt to separate the sources in order to better understand each emission phenomenon, the samples were taken under optimal conditions to eliminate the exhaust gases. The conditions under which the sampling procedures were performed were, firstly, for waste unloading, samples were taken at a distance of 5-10 m from the rear of the trucks (unloading area) and at the edges of the open cell, thus 2-3 m under the exhaust pipe outlets. The direction of the wind carrying the VOCs emitted by unloading also removed the exhaust gases from the sampling location. Secondly, for the compaction vehicles, although it was not possible to obtain this favourable wind orientation, the end of the exhaust pipe was about 2 m above the platform of the vehicle while the sampling tube was placed at about 1 m below it, on the vehicle side. Consequently it was protected from the exhaust gases, with the sorbent tube inlet pointing in the direction of the waste surface.

All the measurements were carried out at the same site, which is representative of most modern municipal waste landfills in France and similar regarding both methods of operation and construction to those in other industrialised countries. The landfill is one of the five largest landfills in France: the total amount of MSW entering this site is more than 400,000 tonnes per year. The site was not licensed to accept toxic or industrial waste.

2.2. VOC analysis procedure: quality assurance and control

Desorption of VOCs trapped on sorbent tubes was carried out by sonication for 14 min with benzene-free carbon bisulphide Fluka (#84713), in which *n*-bromododecane Fluka (#16270) was added as internal standard at a concentration of 21.19 mg/L. The tubes were kept in the refrigerator for a maximum holding time of 24 h before analysis.

A carbon tube recovery test was performed, according to the procedure described in standard ISO 16200-1 [28], by the addition on non-exposed sorbent tubes of $2 \mu L$ of a solution at 4 g/L in each of the compounds analysed. The recovery reached 100% for most of the compounds (heptane, trichloroethylene, tetrachloroethylene, benzene, toluene, ethylbenzene, *m,p,o*-xylenes, 1,2,3-trimethylbenzene, mesitylene), while values different from 100% were 97% for limonene, 96% for α - and β -pinene, 93% for octane, 90% for nonane, 86% for decane and 83% for undecane. The results presented take account of the different desorption rates.

VOC analysis was carried out using an Agilent Technologies 5890 gas chromatograph fitted with a 5973 mass selective detector. The GC capillary column used for all the analyses was a 60-m J&W DB-5MS (diphenyl copolymere (5%) and dimethyl (95%) siloxane) column, 1 μ m film thickness, 0.257 mm i.d. The GC was equipped with a split/splitless injection port operating in splitless mode. The column oven temperature program was the following: 2 min at 36 °C, then a ramp at 5 °C/min until 260 °C. The carrier gas was helium at a flow-rate of 1 mL/min. The mass spectrometer was used in electron impact mode, with ionisation energy of 70 eV. It was operated at full scan in the *m/z* range of 20–300. The filament of the mass spectra was cut off for 12 min (elution of solvent in splitless mode). Compounds were identified by comparison of the mass spectra with those of the NIST (USA) 98 library.

The GC–MS was calibrated using two EPA standard solutions (EPA TO-1 Toxic organic MIX 1A and 1B) and one standard solution prepared in our laboratory. For each solution five calibration points were used.

The mixtures, prepared in methanol, EPA Mix 1A and EPA Mix 1B each had a concentration of 2000 μ g/mL for each compound. The mother solutions of 45.5 mg/L (EPA Mix 1A) and 60.4 mg/L (EPA Mix 1B) were prepared and then diluted to obtain, respectively, five daughter solutions of 23.6, 18.4, 13.1, 7.7 and 3.2 mg/L (EPA Mix 1A) and 22.3, 17.2, 12, 6.5 and 3 mg/L (EPA Mix 1B). The EPA Mix 1A solution contained benzene, ethylbenzene, heptane, heptene, methylethylbenzene, toluene, *m*, *p* and *o*-xylene compounds while the EPA Mix 1B solution contained 1,2-dichloropropane, 1,3-dichloropropane, chlorobenzene, trichloroethylene, and 1,2-dibromoetane.

Dilutions were made of the solution prepared by weighing in our laboratory, resulting in concentrations of 27.6, 18.5, 12.7, 5.8 and 3.7 mg/L. This solution contained the following compounds: dodecane, undecane, decane, limonene, α and β -pinene, 1,2,3trimethylbenzene, mesitylene, nonane and octane. As several calibrations of GCMS were performed during the whole study, the composition of our standard solution was completed at a later date by other compounds such as 2-butanone, 1-butanol, isopropanol and hexane.

Towards the end of the study, in order to obtain a larger panel of VOCs, another EPA 524.2 solution was used for the calibration of GCMS with a total of 36 compounds, each at a concentration of $200 \,\mu$ g/mL. In addition to the compounds already mentioned, the EPA 524.2 solution also contained trichloromonofluoromethane, 1,1-dichloroethene, 1,2dichloroethene, chloroform, bromochloromethane, chlorobenzene, propylbenzene, etc.

In the GC–MS program, a heating speed of 5 °C/min was used. At this speed the separation between some peaks was poor (e.g. *m* and *p*-xylene; β -pinene and decane) though good at 1 °C/min for *m* and *p*-xylene or 2 °C/min for β -pinene and decane. The heating speed of 5 °C/min was kept however for all the analyses in order to limit their duration. A proportionality factor was then calculated for the poorly separated peaks, on the basis of the areas (obtained at 1 and 5 °C/min and 2 and 5 °C/min, respectively) of the peaks with the retention times closest to those of the poorly separated peaks. The proportionality factor obtained in this way was multiplied by the surface of the clearly separated peak at 1 or 2 °C/min in order to obtain the surface at 5 °C/min.

The detection limit of our analytical system was calculated as being twice the background signal of the chromatogram and it was seen to vary as a function of the compound (e.g. $0.05 \,\mu\text{g/m}^3$ for toluene and 0.5 for limonene).

Regarding the replicability of the measurements, three samples were collected synchronously at a fixed sampling location. It was found that the relative standard deviation of the concen-



Fig. 1. Typical chromatogram of VOCs evolved from open cell. 13.79 heptane, 16.89 toluene, 20.79 ethylbenzene, 21.12 *m*-xylene, 21.18 *p*-xylene, 22.11 *o*-xylene, 25.67 decane, 27.25 limonene, 29.17 undecane, 35.48 tridecane as internal standard for another study, 42.95 bromododecane as internal standard for this study, where the number preceding the name of compounds represents the retention time.

tration for each target analyte was less than 10%. By the way, ASTM [29] gives an uncertainty of about 15% for all the analytical chain, starting with the sampling by pre-concentration on sorbent tubes and ending with the GC–MS analysis.

The measurements of VOCs in the background air were also performed and clearly showed that the main source of VOC emissions is the open cell since the analyses carried out in the wind coming from the open cell (downwind) indicated the presence of VOCs, whereas those carried out in the background air (upwind of the landfill) indicated the absence of VOCs even at periphery of the site.

The compounds investigated throughout the study were: heptane, octane, nonane, decane, undecane, trichloroethylene, tetrachloroethylene, benzene, toluene, ethylbenzene, *m*-, *p*- and

o-xylene, 1,2,3-trimethylbenzene, mesitylene, α - and β -pinene, and limonene.

Fig. 1 shows a typical chromatogram (with the targeted VOCs) obtained for landfill gas sampled above an open cell.

3. Results and discussion

3.1. Choice of sampling flow

Preliminary tests were performed on site, at the edge of an open cell, using 2 different sampling rates and the same sample volume/tube: (i) 1 sample was collected through the tube "A" with a flow rate of 0.083 L/min during 120 min (sampling volume of 9.97 L); (ii) 8 different samples were



Fig. 2. VOC concentrations obtained at the side of an open cell using two different sampling flow rates (with same volume of sampling/tube).

taken successively, and in parallel with the sampling on tube A, with a flow rate of 0.63 L/min (sampling time/tube of 15 min, an average sampling volume per tube of 9.84 L) and a total time of 125 min for the 8 samples. In this case (total time of 125 min) an average concentration per compound was calculated with the 8 samples. The results obtained with both sampling procedures are presented in Fig. 2.

The VOC concentrations were quite close for heptane, trichloroethylene, decane, limonene, toluene and tetrachloroethylene. Of the 14 compounds quantified it can be observed that the sampling procedure with a high flow rate provided four more compounds than the sampling procedure with a low flow rate. The four additional compounds are: octane, *p*-xylene, *o*-xylene and undecane. Other compounds (ethylbenzene, *m*-xylene, nonane, α -pinene) were trapped more efficiently by the pump with a low flow rate. Certain variations were probably due to interruptions of the sampling procedure caused by changing the tubes every 15 min for the pump with a high flow rate.

Sampling at a strong flow rate was chosen throughout the study for the following reasons: (i) to obtain information on the evolution of the concentrations through time, and on the presence of "pollution peaks" (i.e. strong concentrations obtained in very short times); (ii) the higher the flow rate, the greater the depression at the entry of the sorbent tube is, making it possible to maintain a constant flow rate even in strong winds; (iii) a flow rate of about 1 L/min is closer to human respiration conditions, thereby validating the comparison to the TWA standards established for workers (see Section 3.3).

In conclusion, long sampling periods with low flow rates can be used to obtain a global view of VOC emissions of a MSW landfill. However, it is necessary to use shorter sampling periods with high flow rates if the aim is to obtain more information concerning the source and the evolution of VOCs throughout landfill site management and operation, by taking into account the influence of various parameters (e.g. meteorological parameters).

3.2. VOC measurements

Two types of measurements were carried out: (i) as a function of time and meteorological parameters; (ii) as a function of activity: spreading and compaction of waste (area called "cells" or "open cells"), discharging of waste (area called "truck"), on the compaction vehicles (area called "vehicle").

3.2.1. Variations of VOC concentrations during the course of the day

Several series of measurements were performed at the same place in wind carrying the VOCs emitted by the open cell.

The results obtained on April 7 and May 23 (see Section 3.2.1.1) provide the concentrations obtained for each VOC. These values were the highest of all the measurements and thus permitted observing significant variations even for the smaller quantities of VOCs. The temperature was plotted for the session of May 23 which constituted a singular case for this parameter (a temperature increase of $20 \,^{\circ}$ C in 1 h).

The quantified VOC concentrations were then totalled for each day of sampling (see Section 3.2.1.2) in order to obtain a clearer picture of the influence of meteorological and site operating parameters.

3.2.1.1. Variation of concentrations for each VOC. Ensuring measurement continuity throughout an entire day is difficult since wind conditions (direction and speed) must remain as stable as possible to ensure that the parameters do not all vary simultaneously. This led us to select the most representative series of measurements carried out at the edge of an open cell on April 7 and on May 23. For these measurements, the sampling locations were much closer to the upper layer of waste than those of the other measurements, thereby explaining the high concentration measurements. The results are synthesised in Figs. 3 and 4, respectively. A continuous layout was selected to connect distinct points as it highlights variations of VOC concentrations more clearly.

Fig. 3 (measurements of April 7) shows the evolution of VOC concentrations which appear close for all compounds, with three high peaks of concentrations at about 11 p.m. and 11:50 p.m. for tetrachloroethylene, heptane and toluene. These concentrations can be explained by the arrival of trucks loaded with waste containing these compounds and by intensive compaction vehicles activity which stirred up the waste. The VOC emissions (type and quantity) vary as a function of the origin of the waste, espe-



Fig. 3. Evolution of VOC concentrations as a function of sampling time (morning, April 7).



Fig. 4. Evolution of VOC concentrations as a function of sampling time (whole day, May 23).

cially in the case of a dump taking in household waste as well as standard industrial and commercial waste, as in the case of the site studied.

Since the temperatures on April 7 were low with constant atmospheric pressure, the main parameters liable to influence the evolution of concentrations of VOCs and the diffusion of the latter into the atmosphere were the activities of the trucks unloading and waste compaction vehicles and the wind speed. These parameters often occur on landfill sites. It is interesting to note that all the compounds react in a homogeneous way to these phenomena, despite sometimes strong concentrations observed for one or more compounds.

Certain compounds were present in all the samples, the highest measured concentrations ($\mu g/m^3$) being: 2480 for heptane, 1200 for toluene, 678 for decane and 726 for limonene. Trichloroethylene was present in half of the samples with a maximum of 699 $\mu g/m^3$. Tetrachloroethylene showed a maximum concentration of 2990 $\mu g/m^3$. The least concentrated compounds were detected irregularly (octane, *p*-xylene, *o*-xylene and undecane).

Concerning the measurements carried out on May 23, the temperature was measured in situ every hour and is shown along with the evolution of VOC concentrations during the day in Fig. 4.

Analysis of the evolution of VOC concentrations according to temperature shows a strong increase of VOC concentrations when the temperature exceeded approximately 15 °C. The fact that the increase of VOCs concentrations occurred during a slack period of waste delivery (11:30 a.m.-1:30 p.m.) and its magnitude shows that this rise in concentrations was solely due to the increase in temperature. This interpretation is also backed up by the fact that the VOC concentrations varied little in the afternoon (stable temperature) with a slight increase of concentrations of all the VOCs at about 2:30 p.m., which is when the compacting engines renew their activity and the trucks arrive to unload waste. It was noted that when the activity of truck unloading and waste compaction vehicles decreased, VOC concentrations also decreased. Generally, it was noted that the trucks unloaded without interruption during the morning (6:30-11:30 a.m.). Then the trucks arrived more sporadically with intervals of about 15-20 min and longer between 2 successive unloading, especially at lunchtime and at the end of the afternoon. The activity of the compaction vehicles was roughly proportional to the quantity of waste brought in by the trucks, with the additional activity of levelling the surface of the waste to make room for further unloading.

The variations of VOC concentrations observed in the morning can be explained by the variation of the type of waste unloaded by the trucks. The most characteristic example relates to a higher concentration of tetrachloroethylene observed around 8 a.m. and a higher concentration of trichloroethylene at about 10:20 a.m.

The concentrations decreased at the end of the day. This can be explained by the major reduction of waste discharge and compaction activities, but also by a slight increase of wind speed, leading to a dilution of VOCs concentrations.

The highest concentrations $(\mu g/m^3)$ were measured for the following compounds: tetrachloroethylene (9810 and 6920), toluene (8230), limonene (4545), *m*-xylene (3980) and trichloroethylene (3680).

The concentrations obtained on May 23 were systematically much higher than those obtained on April 7. This difference was mainly due to meteorological conditions, i.e. lower temperatures that limited the VOC emissions on April 7 and stronger winds that increased the diffusion of the VOCs and correspondingly decreased their concentrations.

3.2.1.2. Variations of total VOC concentrations. The results obtained for the four sampling sessions (days) are reported in Fig. 5 which presents for each of the charts the total VOC concentrations quantified as a function of sampling time.

Firstly, there is a relation between the average of concentrations per day and the vertical distance between the upper layer of waste and the sampling location, as the VOC concentrations decreased as the distance increased (e.g. 12,800 μ g/m³ and 1 m for May 23; 364 μ g/m³ and 8–10 m for June 12). In our opinion, this can be explained by the dispersion of VOCs as soon as they are emitted, even though this distance is directly related to the cell filling level: the filling level is also related to the number of temporary soil covers buried in the waste and the depression of the waste due to the connection with the general biogas circuit.



Fig. 5. Total concentrations of VOCs ($\mu g/m^3$) as a function of sampling time for four different sampling days.

Regarding atmospheric pressure, this varied little during each session (anticyclonic conditions) and regularly decreased from morning to night (Table 2). It therefore had little impact on the emission of VOCs by the open cell.

The samples of short duration (15 min) taken on April 7 show the rapid variation of concentrations due to the diversity of the wastes unloaded (the other parameters varied less rapidly), as has already been mentioned (Section 3.2.1.1).

Sampling for the session of April 30 started very early (5:30 a.m.) with dense fog (humidity of 95%) that confined the VOCs emitted to the level of the open cell. The highest concentrations obtained for the first sample in comparison to the second and third samples can be explained by the start of activity of the compaction vehicles (6:00 a.m.) which, by agitating the waste, allowed the VOCs formed since the preceding day and during the period of inactivity of the compaction vehicles, to escape. The concentrations increased at the end of the morning with the increase of temperature ($2.7 \,^{\circ}$ C at the beginning of measurements and 18.5 $^{\circ}$ C at the end of measurements) and perhaps also with the arrival of waste with higher VOC emissions. The wind had no influence on these VOC emissions, since its direction and speed remained constant until the end of measurements.

The session of June 12 allowed us to highlight the influence of activity on the cell in operation (i.e. reduction of the total concentrations of VOCs, in parallel with the reduction of the activity of the compaction vehicles and trucks) since all the other parameters (temperature, wind speed, atmospheric pressure, humidity) were relatively stable. This reduction of concentrations was clearly observed after 16:00 h on 12 June and 23 May.

The peak observed on the plot of the total VOC concentrations for the session of May 23 was probably due to the very considerable and rapid increase of external temperature (~ 20 °C in 1 h) since it occurred during a period of very low activity of trucks unloading waste and compaction vehicles.

3.2.2. Variation of VOC concentrations with activity on the site

Different activities that take place on a landfill site (unloading and compaction of waste, opening of cells, etc.) frequently led to high VOC emissions and thus strong odours. It was therefore considered useful to take measurements in order to characterise the concentrations of VOC emissions as a function of these different activities.

Two additional VOC emission parameters require definition: (i) the flow of emissions characterising the source and thus its global impact on the environment (contribution to the greenhouse effect) and (ii) concentrations close to the emissions, values that characterise the effect on people present at these points and that depend on both the flows emitted and their diffusion. For this study, we systematically chose situations of high emissions (high temperature) and low diffusion (light wind).

Three different areas of activity were selected: the waste storage area with spreading and compaction of fresh waste; the truck unloading area; the area adjacent to the compaction vehicles.

3.2.2.1. Storage area with spreading and compaction of fresh waste. The measurements already mentioned (April 7, April 30, May 23, June 12) were performed in this area.

3.2.2.2. Truck unloading area. The truck unloading area is on the edge of the open cell, with the waste being tipped directly into the cell. More information about the sampling location in this

area is presented in Section 2.1. Since this area is narrow, only 10 m wide, it means that throughout the morning only two trucks can unload at the same time, with one or two trucks waiting in a queue to enter the area. Thus there is a continuous flow of waste into the cell.

The results of the measurements made on May 23 in this area are given in Table 4 in comparison with those of the open cell presented previously.

To compare the two areas (open cell and truck area), average values were calculated over the morning and the afternoon.

In most cases the values obtained (15 VOCs out of 17 VOCs monitored) were higher in the truck unloading area, clearly showing that the fresh waste already contained VOCs. This phenomenon was minimised by the VOC "peak" over the open cell, due to the temperature increase that did not occur in the truck unloading area. Indeed, the trucks were unloaded immediately on arrival and transport did not lead to a fast rise in temperature under the action of the sun, contrary to the open cell.

The variety of the waste brought in by the trucks caused a far more random evolution of concentrations in the truck unloading area than at the surface of the open cell, even if the waste is spread. Spreading mixes the sources of VOC emissions and thus "dilutes" strong concentrations.

There was a peak concentration for toluene $(7880 \ \mu g/m^3)$ from 11:30 a.m. to 12:30 p.m. in the area located next to the trucks tipping the waste and another peak concentration $(8230 \ \mu g/m^3)$ from 12:37 p.m. to 1:37 p.m. at the edge of the open cell. This was probably due to the fact that the waste tipped by the trucks was spread mechanically over the surface of the open cell, approximately an hour after being tipped.

The strongest concentrations (μ g/m³), measured next to the trucks corresponded to the following VOCs: tetrachloroethylene (7320), toluene (7880), limonene (3270), *m*-xylene (2510), trichloroethylene (2470) heptane (1730), ethylbenzene (1340) and decane (1290). These are the compounds found most often at high concentrations, which is hardly surprising given that they are frequently used as solvents, cleaning and degreasing products, perfume additives, etc.

By comparing the results obtained adjacent to the trucks and those obtained at the edge of the cell in operation, the same VOCs forming most of the emissions can be observed, highlighting that the emission was mostly due to fresh waste.

3.2.2.3. The area adjacent to compaction vehicles. The availability of access to the compaction vehicles allowed us to perform two series of measurements in parallel on July 23: one at the edge of the open cell and the other on the compaction vehicle. Three samples were taken at the same time for each location in the morning.

These conditions provided us with an optimal window for carrying out the measurements: a temperature over 20 °C, and a period in which a large quantity of waste arrived continuously.

Following previous works [30] carried out on another site, that highlighted the diversity of the VOCs emitted and the variations of concentrations due to the arrival of waste, we decided to increase the number of compounds quantified for these measurements in order to confirm this observation and obtain more information from the analyses.

The comparisons of the "vehicle–cell" results for the six samples taken in parallel (3×2) are presented in Figs. 6–8.

For the first and third sample, the concentrations were on average five times higher next to the compaction vehicle than at the edge of the open cell and 20 times higher for the second sample. However, if the results of the two areas are compared compound by compound, it can be seen, for example, that concentrations are 200 times higher for tetrachlorethylene next to the compaction vehicle (for the second sample) and 40 times higher for trichloromonofluoromethane next to the compaction vehicle (for the first sample) than at the open cell. These variations of concentration ratios between the two areas (open cell and waste compaction) for the different VOCs stemming from waste assimilated with household waste clearly highlight the random nature of the corresponding emissions and emissions and their magnitude.

Trichloroethylene was only detected once in the 6 samples. The presence of trichloroethylene, a solvent used for metal cleaning but partially prohibited because of its toxicity, can be explained by the degradation of tetrachloroethylene used for both dry cleaning and metal cleaning. Some authors [2,31] assert that the biochemical breakdown of tetrachloroethylene, occurring via anaerobic hydrogen–halogen substitution, can lead to the formation of trichloroethylene. Older wastes can be brought back to the surface of the open cell by the activity of the compaction vehicle and thus to release the trichloroethylene formed as indicated below.

Tetrachloroethylene was detected five times in the six samples and at relatively low concentrations in comparison to previous analyses.

Other compounds were only detected and quantified near the compaction vehicles. These were: octane, isopropanol, 1-butanol, dodecane, 1,2-dichloropropane, propyl-benzene, mesitylene and β -pinene (detected also only once at the edge of the open cell).

Given that the pumps were installed very close to the source of emission where the concentrations were greatest and the samples were taken at high flow rates, we expected that the breakthrough volume would be reached for certain compounds (alkanes C7–C10, *ortho-* and *para-*xylene, toluene) but this compromise was necessary in order to achieve greater sensitivity for the lower concentrations.

The comparative "compaction vehicle–open cell" measurements showed a greater number of compounds and higher VOC concentrations next to the compaction vehicle. This can be explained by the fact that the compaction vehicle was much closer to the emissive area and the action of agitating the waste combined with tearing the bags containing the waste led to the release of the compounds trapped in them (as much for the waste that had just been tipped as for that from the lower layers). This phenomenon has already been identified by other authors [23].

It would have been interesting to see whether this trend was as prevalent under less favourable emission conditions (lower tem-



Fig. 6. Comparison of compaction vehicle-cell results for the first sample.



NB: For EB and m-xylene compounds, concentrations are 2455 and 1775 µg/m³ (they do not appear in the chart for presentation reasons).

Fig. 7. Comparison of compaction vehicle-cell results for the second sample.



Volatil organic compounds

Fig. 8. Comparison of compaction vehicle-cell results for the third sample.

Table	4
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Averages of concentrations (μ g/m³) calculated over the morning and the afternoon for two exposure areas (open cell and truck) — May 23

Compound	Measurement area					
	Truck	Open cell	Truck	Open cell		
	Morning ^a		Afternoon ^a			
Heptane	910	743	1100	977		
Trichloroethylene	929	1650	670	266		
Toluene	4150	2190	1850	2220		
Octane	72.1	58.4	73.9	56.1		
Tetrachloroethylene	4900	4820	1330	2040		
Ethylbenzene	621	416	1060	740		
<i>m</i> -Xylene	1340	820	1710	1370		
<i>p</i> -Xylene	108	277	582	332		
Nonane	353	238	416	298		
o-Xylene	339	262	488	385		
α-Pinene	315	287	368	209		
Mesitylene	115	86.0	154	97.9		
Decane	780	570	915	680		
1,2,3-Trimethylbenzene	_	_	114	115		
Limonene	2320	1870	1820	1470		
Undecane	238	194	307	213		
Dodecane	20.1	49.7	55.1	19.7		

^a Sampling period.

peratures). Also, another parameter not studied was the duration of storage of the waste in the bags before burial (collection in rural areas or following weekends). It is likely that longer storage periods lead, especially during hot periods, to an increase in the amount of VOCs released during compacting. This supposition is also confirmed by another author [19]. His study shows that the variety and concentration of VOCs evolved depends on the prevailing conditions such as time of waste exposure, load and weather. This author also affirms that when waste accumulates in bins under unforeseen circumstances, some compounds produces may exceed olfactory and safety thresholds representing a source of potential health impact.

To conclude, we thought that it would be interesting to compare our results (type and concentration of VOCs) with the findings of other similar works. Zou et al. [5] found that aromatics are the dominant VOCs in landfill air (e.g. $202 \,\mu g/m^3$ for toluene, $97 \,\mu g/m^3$ for (m+p)-xylene, $52 \,\mu g/m^3$ for ethylbenzene).

Toluene is one of the most predominant components of the aromatic VOCs present in landfill gas as supported by other authors [10,20]. Both toluene and xylenes are solvents widely used in paints, paint thinners, nail varnishes, etc. while ethylbenzene is used in pesticides, varnishes, adhesives and paints [32].

Terpenes, another family of VOCs found in landfill gas, are derived from plant waste, shrubs and vegetable waste but also from fragrant household detergents and air fresheners [2]. One author [33] asserted that terpenes may be biosynthesised for the most part on site during the degradation of organic matter. The same author [33] states that several of these compounds are also widely used and are persistent to biotransformations under the methanogenic conditions found in landfills. Another author [19] found that limonene showed the highest concentrations under all the conditions examined ($757 \mu g/m^3$). Other studies [5,7] found that the maximum concentrations (in $\mu g/m^3$) obtained for

limonene in the ambient air of a landfill site were: 162 [5], 75.9 (fresh waste emissions) and 4.1 (ambient air landfill entrance emissions) [7].

Concerning the organohalogens (trichloroethylene, tetrachloroethylene, etc.), the potential sources are: aerosols, paint remover, dry cleaning agents, dyeing solvents, foam blowing agents, soaps, paint and varnished refrigerators [2]. Davoli et al. [7] found $0.4 \,\mu g/m^3$ for tetrachloroethylene in both fresh waste and ambient air landfill entrance emissions and no trace for trichloroethylene. The maximum concentrations obtained in another study [5] for trichloroethylene and tetrachloroethylene were 24 and 59 $\mu g/m^3$, respectively.

As can be seen the VOC concentrations obtained in the ambient air of a landfill site by other authors [5,7,8,10,16,20] are generally lower than those obtained in this study. This could be explained by the fact that our measurements were performed very close to the source (open cell) and thus dilution with air was minimised. On the other hand, it is difficult to compare our results with the biogas values found by other authors, since they originate, via forced aspiration without dilution, from all the layers of the waste in the cells in operation and those that have been closed. This explains why the concentrations found in the biogas are higher than those of our results (e.g. maximum values of 225,000 µg/m³ for tetrachloroethylene, 152,000 µg/m³ for trichloroethylene, 287,000 µg/m³ for toluene and limonene [2]).

3.3. Evaluation of VOC exposure concentrations for workers

The measurements shown before permit evaluating the concentrations of pollutants to which the persons present on the site are exposed.

This evaluation does not include the compaction vehicles themselves since the only persons present in this area are the Table 5

Comparison of average concentrations obtained over 8 h^a for two exposure areas (open cell and truck area) with the time weighted average concentrations (TWA) established by INRS—May 23

Compound (µg/m ³)	Measur (averag	ement area e over 8 h)	TWA $(10^3 \times \mu g/m^3)$
	Truck	Open cell	
Heptane	1009	835	2085
Trichloroethylene	851	983	405
Toluene	3088	2471	375
Octane	73	64	1450
Tetrachloroethylene	3257	3684	335
Ethylbenzene	805	662	442
<i>m</i> -Xylene	1428	1256	221
p-Xylene	330	346	221
Nonane	403	306	1050
o-Xylene	431	372	221
α-Pinene	350	272	-
Mesitylene	141	104	100
Decane	871	694	_
1,2,3-Trimethylbenzene	71	72	100
Limonene	2183	1844	_
Undecane	292	231	-
Dodecane	41	37	-

- no data available for these compounds.

^a The samples were taken over a total period of 9 h but averages were formulated for 8 h by eliminating the last sample taken at the end of the day.

drivers of the vehicles who operate in pressurised cabs supplied with air purified by an active carbon filter.

This leaves the truck tipping area and the waste spreading area to be taken into account. The samples taken on May 23 in the truck tipping area and at the edge of the open cell were taken into account for this evaluation.

Table 5 shows the average concentrations obtained over 8 h compared with the TWA concentrations established by INRS (National Institute of Sanitary Risk/France) [34]. These are time weighted average concentrations intended to protect workers against long-term effects, measured or estimated over an 8 h work-shift.

We note that no value exceeds the TWA. Conformity with the limit values however does not mean an absence of health risk [35]. Indeed:

- the methods used to establish them vary from one country to another;
- these values are only valid for pure single compounds;
- the determination criteria vary from one substance to another;
- the exposure conditions play a primordial role.

Thus labour legislation was respected (conformity with TWA) on the site studied at the time of sampling. However, these results cannot be used to judge health risks for populations outside the site. Consequently, this work must be completed by a study of the dispersion of VOCs outside the site to evaluate the impact on the closest dwellings, despite the fact that concentrations decrease considerably with distance from the source of emission. This work is being written at present and

will be presented in a forthcoming publication. It must then be completed by an evaluation of the corresponding health risks.

4. Conclusion

The bibliographic study showed that much research has been devoted to the identification and quantification of VOCs in the biogases of waste dumps (industrial, household waste, etc.), though few studies have been carried out on the ambient air of such sites [5,7,8,10,16,20].

This work gives relevant information about the VOC concentration measurements on a fresh waste open cell as a function of sampling time and area of activity (unloading, spreading and compaction of waste). We chose relatively stable atmospheric conditions for all the measurements (no rainfall and almost constant pressure, wind force and direction during the sampling) and distances of several meters between the sampling point and the layer of waste. These restrictions obviously limited the sampling sequences and their duration, but this was the necessary condition for obtaining information on these emissions.

The pollution peaks observed for certain compounds in two series of measurements carried out at the edge of an open cell (May 23 and April 7) appear to be caused by variations in the nature of the loads in the trucks transporting the waste. Tetrachloroethylene and heptane were observed with maximum concentrations of 2990 and 2480 μ g/m³, respectively, in the area of the open cell during the morning of April 7 and of 9810 and 3680 μ g/m³, respectively, during the morning of May 23. The high concentrations of these compounds in the waste unloaded are also linked to conditions favouring their emission and minimising their dispersion (i.e. low distance between the sampling location and the upper layer of waste due to the cell-filling level).

Most VOCs were measured at greater concentrations in the truck unloading waste area compared to the open cell. One example is toluene which was measured at $7880 \,\mu g/m^3$ close to the truck area and $3630 \,\mu g/m^3$ over an open cell, with both measurements being performed at the same time.

Another major contribution stems from the compaction vehicles that, by agitating and compaction of waste, tear the bags and boxes containing waste loaded with VOCs, and by consequence release them into the ambient air. More compounds and higher VOCs concentrations were detected next to the compaction vehicle than in the open cell area on July 23 (e.g. $1090 \,\mu g/m^3$ compared to $206 \,\mu g/m^3$ for limonene; $668 \,\mu g/m^3$ compared to $273 \,\mu g/m^3$ for toluene, etc.). The concentrations were on average 5–20 times higher next to the compaction vehicle than at the edge of the open cell.

Temperature and wind also have an impact on the variation of VOC concentrations: increases in temperature increase the release of VOCs (higher concentrations obtained on May 23, at about 13:00 h, due to the very high and rapid increase of temperature) while higher wind speeds favour their dispersion and thus dilution (measurements of April 7).

The highest concentrations of VOCs in most of the measurements were obtained for: tetrachloroethylene, heptane, trichloroethylene, toluene and limonene. The results obtained show that, for the site studied, conformity with the time weighted average concentrations (TWA) established by INRS for occupational purposes was respected but it not necessary means absence of the health risks for workers. The method formulated must now be repeated at other periods and at other places at the same site, as well as other sites to obtain more in-depth characterisation of the general exposure of workers to VOCs in household waste storage installations.

In addition, as these works are to be completed by a study of VOC dispersion outside the site, they will then be used not only as the basis for evaluating the health impact of VOCs on people working on landfill sites but also for the health risks for the surrounding population.

5. Recommendations

The most efficient solutions for limiting the release of VOCs into the atmosphere will be those that act on the most pollutant areas: the truck tipping area and the waste compaction area. One of the solutions would be to install vaporizers on the truck tipping platforms and installing mist sprayers (with very small droplets to limit the water added to the waste) on the compactors. Another solution would be to optimise the activity of the compactors and therefore their movements, which could be done at no extra cost.

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