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Improvement in 8h-sampling rate assessment considering meteorological parameters variability for biogas VOC passive measurements in the surroundings of a French landfill

Marie Verrièle^{a,*}, Nadine Allam^b, Laurence Depelchin^a, Laurence Le Coq^b, Nadine Locoge^a

^a Mines Douai, SAGE, 941 rue Charles Bourseul, BP 10838, F-59508 Douai Cedex, France

^b LUNAM, Mines Nantes, GEPEA, CNRS, UMR 6144, 4 rue Alfred Kastler, BP 20722, FR-44307 Nantes Cedex 3, France

A B S T R A C T

Passive sampling technology has been extensively used for long-term VOC atmospheric concentrations' monitoring. Its performances regarding the short-term measurements and related to VOC from biogas were evaluated in this work: laboratory scale experiments have been conducted in order to check the suitability of Radiello[®] diffusive samplers for the assessment of 8 h-VOC levels in highly changeable meteorological conditions; in a second step a short pilot field campaign was implemented in the vicinity of a West-French landfill. First of all, it was assessed that amongst a diversified list of 16 characteristic compounds from biogas, mercaptans, some halogenated, oxygenated compounds and terpenes could not be measured accurately by this passive technique either because they are not captured by the sorbent or they are not quantitatively desorbed in the chosen mediated analytical conditions. Moreover, it has been confirmed that sampling rates (SR) related to isopentane, THF, cyclohexane, toluene, p-xylene and n-decane are influenced by environmental factors: the main influence concerns the wind speed. From 2 m s^{-1} , when the velocity increases by 1 m s^{-1} , the SR increases from 12 to 32% depending on the COV (considering a linear dependence between 2 and 7 m s^{-1}). Humidity has no effect on SR, and temperature influence is rather limited to less than 3% per degree. A comprehensive uncertainty estimation, including uncertainties linked to meteorological changes, has led to global relative uncertainties comprising between 18% and 54% from one VOC to another: a quite high value comparatively to those obtained without considering meteorological condition influences. To illustrate our results, targeted VOC were quantified in the field, on a single day: concentrations range between LD to $3 \mu\text{g m}^{-3}$: relatively very low concentrations compared to those usually reported by literature.

Keywords:

Biogas volatile organic compounds
Passive sampling
Experimental sampling rates
Meteorological parameters
Landfill

1. Introduction

European current landfill sites offer more and more promising solutions to the problem of fugitive emissions consisting in capturing the biogas produced herein through a network collector system, installed in the core of deposited waste, and leading to energy production. Despite optimized waste cover systems, a part of the landfill gas is still emitted to the atmosphere. Biogas is mainly composed by CH_4 and CO_2 , two green gases, but it also contains various other volatile organic compounds (VOC): aromatics, hydrocarbons, aldehydes, alcohols, carboxylic acids, amines, halogenated compounds, terpenes, reduced sulfur compounds, esters, etc. [1]. Most of the studies that report VOC concentrations in the vicinity of landfills are focused on the odorous

compounds affecting directly public health and comfort [2–5]. Without being exhaustive, Table 1 gives an overview of typical VOC levels measured in the vicinity of landfills in Korea, China, Turkey [3,6–8] and over a waste open cell in a French landfill [9]: the concentrations are generally spanning several degrees of magnitude, from units to hundreds of $\mu\text{g/m}^3$.

Impact of landfill sites on their vicinity is evaluated by VOC concentrations measurements: online monitoring methods using self-contained analyzers (Fourier Transform Infrared spectroscopy, Diode Laser Adsorption Spectroscopy or compact gas chromatography) [10–15], instantaneous samplings [2] or pre-concentration passive and active samplings with differed chromatography analysis can be set up [16]. Online monitoring provides high-time-resolution concentration data but implies heavy instruments; Instantaneous sampling (in a plastic bag or canister) which can be done in multiple sampling points is easier to use but still questionable: it could be unrepresentative since samplings are taken in short periods (at most 1 h) [2], induce some conservation

Table 1
Typical VOC levels measured in the vicinity of landfill site.

Compounds	Sampling site	Concentration ($\mu\text{g}/\text{m}^3$)	Compounds	Sampling site	Concentration ($\mu\text{g}/\text{m}^3$)
Toluene	Dae Gu (Korea) [8]	4.9–65	Pentanoic acid	Hangzouh (China)	0.02–0.12
	Shanghai (China) [7]	12–175		Izmir (Turkey)	0.07–5.0
	Hangzhou (China) [3]	1.9–60			
	Izmir (Turkey) [6]	1.6–48			
	Open cell (France) [30]	8230			
m,p-Xylene	Dae Gu (Korea)	0.4–11	Pinenes	Hangzhou (China)	0.004–0.02
	Shanghai (China)	44–152			
	Hangzhou (China)	0.02–58			
	Izmir (Turkey)	0.4–10			
1,1,2-Trichloroethene	Shanghai (China)	0.05–9.2	Limonene	Open cell (France)	4550
	Open cell	3680			
1,1,2,2-Tetrachloroethene	Open cell (France)	9810	Dimethylsulphide	Shanghai (China)	1.5–138
Hexanal	Shanghai (China)	11–32	Methylamine	Shanghai (China)	1.8–96
	Izmir (Turkey)	0.47–5.9			
Ethylbenzene	Izmir (Turkey)	0.15–4.9	Dodecane	Open cell (France)	50
	Open cell (France)	416			

difficulties and require for low concentrations measurements an additional pre-concentration step on SPME fibers [3,19] or on solid trap. Sampling methods with pre-concentration are based on adsorption/desorption on solid supports followed by analysis using the thermal desorption method coupled with GC-FID/MS. Passive sampling, versus active sampling, is often preferred since it makes possible the implementation of samplers on a large scale, even in hard-to-reach and remote areas, resulting into a large monitoring network [20]. Many samplers are commercially available, such as Perkin-Elmer tubes, OVM badges, SKC badges, Orsa 5 samplers, Radiello or have been recently developed [21,22]; SR are generally provided by the manufacturers for standard conditions. They are currently used not only for indoor measurements [23–25], atmospheric surveys in urban, industrial [26–29] or landfills [30] sites, but also for personal exposure measurements [31–34]. Passive samplers are cost-effective and easy to use; nevertheless they could present two critical drawbacks concerning the SR control and the sampling duration. In fact, the main limitation of passive technique is the non-regulation of the sampling flow. Under ideal behavior, the sampling rate is only based on the analyte's molecular diffusion described by Fick's first law, and consequently, only indexed on the sampler geometry (cross section of the diffusion area) and on the diffusion coefficient specific to each targeted compound. But in reality, for average concentration calculation, sampling rate (SR) has to be estimated experimentally since it also depends on the weather conditions and the sampling time [27,35,36] and the adsorbent used. The second key point is the sampling duration which is recommended to be comprised between 8 hours to 14 days, but a 7-day exposition duration is often needed for the measurements of low concentrations, which is definitely too long compared with the emission dynamic in landfill sites.

Our research group used to work with the Radiello[®] sampler, suggests in an up to date article [36] a thinner diffusive body which could reduce sampling period. In this work, we propose to study and validate the possibility to sample VOC in the atmosphere of a landfill site for 8 h time period using 2 types of diffusive bodies and under highly changing meteorological conditions. The targeted VOC SRs have been determined studying the influence of environmental parameters (humidity, wind speed and

temperature); the performances of the sampler in wind speed conditions over 3 m s^{-1} are assessed for the first time in this paper which also include a comprehensive uncertainty estimation linked to large meteorological changes. Finally, in order to illustrate the feasibility of the sustained method, targeted VOC were quantified in a French landfill: only a single day measurement is presented, since other seasonal field campaigns are scheduled for further works.

2. Material and method

2.1. Radial diffusive sampler

The Radiello[®] sampler (code 145) is composed of several parts: an adsorbing cartridge, a diffusive body, a supporting plate and an adhesive label. The adsorbing cartridge is a stainless steel net coaxial cylinder (60 mm long, 4.8 mm diameter and 100 mesh hole size) filled with $300 \text{ mg} \pm 10 \text{ mg}$ of 35–50 mesh Carbograph 4 (graphitized carbon black) which is inserted in the diffusive body: a microporous polyethylene membrane. Two kinds of membranes are available: a white (code 120) and a yellow diffusive body (code 120-2) characterized respectively by a diffusive path length of 18 and 150 mm, a thickness of 1.7 and 5 mm and a pore size of 5 ± 5 and $10 \pm 2 \mu\text{m}$. The thin diffusive body is recommended for shorter exposure time (higher SRs, several tens of $\text{cm}^3 \text{ min}^{-1}$) whereas the thick membrane should be used for long time exposure (about 2–3 times lower SRs comparing to the thin one). Compound concentrations are calculated using Eq. (1) derived from Fick's law:

$$C = \frac{m - m_b}{t \cdot \text{SR}} \quad (1)$$

where m is the sampled mass of compound (μg) during the sampling time t (min) for an atmospheric concentration C ($\mu\text{g m}^{-3}$), m_b is the mass of compound in a non-exposed cartridge (blank mass value) and SR the sampling rate ($\text{cm}^3 \text{ min}^{-1}$).

3. Exposure chamber, standard gas and design of experiments

3.1. Exposure chamber

The exposure chamber consists of a glass ring tube with a $74 \times 88 \text{ cm}^2$ size, a 15 cm diameter and a 51 L capacity placed in a thermostatic enclosure of 990 L (M 54054 manufactured by Votsch). An inductive fan (Papst P/N 5112N) is set up to regulate the air velocity inside the chamber between 0.3 and 10 m s^{-1} . Humidity is regulated by varying both the dry and humid airflows. The diffusive samplers are placed perpendicularly to the dynamic airflow. The schematic drawing of the experimental setup can be found in Roukos et al. [36].

3.2. Standard gas

The exposure chamber is supplied by a VOC mixture coming from a set of three standard gas cylinders. Their composition was based on the biogas collected in the network system of the studied landfill, they contain 16 compounds with loads spanning between 2 and 22 ppm in nitrogen: isopentane (2-methylbutane), n-decane, cyclohexane, 2-butanol, trichlorofluoromethane, dichloromethane, 2-butanone, toluene, p-xylene, 4-isopropyltoluene, ethyl butyrate, tetrahydrofuran (THF) (first cylinder); limonene, alpha-pinene (second cylinder); and isopropylmercaptane and tert-butylmercaptane (third cylinder). VOC flow coming out of the standard gas bottles is diluted in two steps with purified air using mass flow controllers. Upstream of the exposure chamber inlet, VOC charged airflow is mixed with a humidified air in varying proportions depending on the desired humidity in the chamber. VOC concentrations in the exposure chamber are monitored continuously using an on-line VOC analyzer (Airmo VOC C6C12-Chromatotec) which is calibrated with a UK national gas standard from NPL (National Physical Laboratory, London, UK). The concentrations range from 2 to $15 \mu\text{g}/\text{m}^3$ depending on the compound.

3.3. Design of experiments

In each trial, two sets of 4 identical diffusive samplers, equipped with thin or thick bodies were exposed in the atmospheric chamber.

8 h-standard SRs were determined from 2 trials, for thin and thick bodies under standard chamber conditions: $25 \pm 0.5 \text{ }^\circ\text{C}$, $45 \pm 5\%$ RH and $2 \pm 0.1 \text{ m s}^{-1}$. A design of experiments was used to observe the influence of three environmental factors (T, RH and air velocity) on the thin diffusive body SR. It permits the simultaneous evaluation of several factors and their interactions with a minimum of experiments. A fractional factorial design (FFD) was retained with three factors at two levels of evaluation (low and high); each experiment was repeated twice. For the thick body, SRs were determined for 5 air velocity conditions ($0.5, 1, 2, 4$ and 7 m s^{-1}) at a fixed temperature and relative humidity ($25 \text{ }^\circ\text{C}$ and 50%). In addition, SRs were determined for 3 temperatures (5, 15 and $25 \text{ }^\circ\text{C}$) at fixed air velocity and relative humidity (2 m s^{-1} and 50%). Experiments were conducted twice for each condition.

4. Analytical instrumentation and analytical procedure

The sampled cartridge analysis uses a thermal desorption system (TD) (Unity2-Markes) coupled to a gas chromatograph (GC/Agilent). It is equipped with an apolar column and a dual detection: a mass spectrometer (MS) and a flame ionization detector (FID). Thermal desorption of VOC is performed in several steps: the sampling tube is desorbed at $350 \text{ }^\circ\text{C}$, VOC released are flushed to a trap. The trap is cooled at $9 \text{ }^\circ\text{C}$ and purged during 3 min with

20 mL min^{-1} helium flow. It is constituted of two adsorbents: Carbotrap C (18.4 mg) and Carbopack B (57.5 mg). In a second step, the trap is heated allowing the VOC to be injected into the column ($105 \text{ m} \times 0.32 \text{ mm} \times 1.5 \mu\text{m}$). The helium flow rate is maintained by the flow column (3 mL min^{-1}). After separation by chromatographic column, the flow is divided between MS and FID into a 10/90 ratio. Adsorbent cartridges need to be conditioned at $350 \text{ }^\circ\text{C}$ before use, and the residual mass average or the mass blank value for each compound of interest is determined by their subsequent TD-GC analysis. The blank mass values are determined for each compound by analyzing 6 unexposed samplers. Adsorbed masses were determined using a calibration curve, based on the analysis of cartridges loaded, following an optimized procedure, by 6 different known masses comprised between 10 and 250 ng. For each level of calibration, $1 \mu\text{L}$ of a liquid standard solution, diluted in methanol, is vaporized in a GC injector at $150 \text{ }^\circ\text{C}$, under a 30 mL min^{-1} helium flow connected during 3 min via an inert capillary glass tube to the sorbent cartridge inserted in a stainless steel tube. All obtained calibration curves following the equation $k_i = \text{area}/\text{concentration}$ exhibit a regression coefficient above 0.97. The intercept, representing the blank value, was ignored ($< 5 \text{ ng}$). The analytical recovery rate has been verified by direct liquid injection for BTEXs in previous work [40], it has been shown that it is equal to 1 ± 0.05 . Moreover for lowest boiling point compounds, a second thermodesorption permits to confirm that more than 95% of the initial adsorbed mass is desorbed in the first heating step. Detection limits (DL) are calculated from the standard deviation of blank values, and 8 h-standard SR. For compounds (isopentane and THF), for which blank values cannot be measured (that is to say under 0.5 ng), the detection limit is estimated from the ratio between signal/noise observed in the analysis of a cartridge loaded with a mass around 1 ng. The repeatability of the analytical method was assessed by the analysis of 7 cartridges loaded with the same mass of each compound contained in the gas cylinders and corresponding to typical masses adsorbed into a field exposed sample tube (hundreds ng).

5. Studied area and sampling strategy for field campaign

A single-day field campaign was conducted on May, 30th 2013. Nine 8 h-sampling points were selected (from 8 am to 4 pm) to evaluate VOC concentrations on site and its surroundings. The studied 'Séché Environment' site is located near to Changé in the West part of France. The site covers an area of 170 ha and receives about 700 thousand tons of non-hazardous-waste per year. The biogas collection network is implemented in the core of the disposed non-dangerous solid wastes and works under depression. The captured biogas, estimated to be more than $2000 \text{ Nm}^3 \text{ h}^{-1}$, is used for energy production on the site: electricity and heat. A site maps is proposed in the Supplementary information (Fig. S1). Sampling was carried under a temperature varying between 6 and $8 \text{ }^\circ\text{C}$. Relative humidity was almost constant (93%) and wind speed varied between 3.1 and 4.2 m s^{-1} until 2 pm and later on between 5.3 and 5.8 m/s^{-1} . The wind was coming from the North-West direction ($290\text{--}305^\circ$). Concentrations and their uncertainties were calculated using standard sampling rates given in the next section of this paper.

6. Results

The analytical procedure, comprising the thermodesorption and the chromatographic analysis stages, was optimized for BTEX, which are fundamental components in the evaluation of air quality. Using this procedure, and after the analysis of 7 tubes

dedicated to repeatability assessment, we noted that only 12 compounds could be detected; mercaptans and some halogenated (dichloromethane, trichlorofluoromethane, isopropylmercaptane, tert-butylmercaptane) are either not captured by the sorbent or not desorbed quantitatively. In the same way, limonene and α -pinene were randomly detected depending on the experiment. Probably, an optimized thermo-desorption method should be implemented. Among the detected VOC, only 6 compounds (isopentane, THF, cyclohexane, toluene, p-xylene and decane) show a Relative Standard Deviation (RSD=standard deviation/average mass) inferior to 10%. Butanol, ethyl-butyrate and MEK have a high RSD which exceeds 45%, while 4-isopropyltoluene presents a RSD lower to 20%. The Radiello[®] sampling technique, coupled to our analytical procedure is not fulfilling with regard to these non-detected compounds (mercaptans and halogenated compounds) and these non-reproducible compounds (mostly oxygenated compounds).

Taken into account these results, the following sections will only deal with the 6 reproducible compounds. Results obtained for the other compounds for which it has been shown a non-reproducible adsorption are still presented in the "Supplementary material", Tables S1 and S2.

6.1. Determination of sampling rates under standard conditions and detection limits

8 h-SRs under standard conditions for thin and thick bodies were calculated according to Eq. (1) and gathered in Table 2, in comparison with 7-day-Radiello standard SRs for thick bodies. The standard deviations associated with SRs of our target compounds are relatively low, indicating a good repeatability of the experiments.

Taking into account these standard deviations, the results obtained in this work for the thick body are in accordance with Radiello one's although the exposure time is significantly shorter, except for decane. Highly lower than Radiello one's, the decane mean SR could be only explained by an uncompleted thermo-desorption. Indeed, a potential competition between compounds is more likely to enable the adsorption of light compounds instead of heavy compounds. As said before, a second thermo-desorption of the sampling tubes was conducted, but still at the same temperature. A higher temperature near to 400 °C could potentially lead to higher SR. Moreover, back diffusion is not likely to occur on short sampling duration: adsorbed masses are quite low (hundreds ng) and ambient concentrations do not significantly vary unbalancing the equilibrium between adsorbed and gas phases. Concerning the thin body results, only toluene and xylenes SR can be compared with our previous work [36]. The toluene SR is significantly higher than the previous one ($58.7 \pm 4.0 \text{ mL min}^{-1}$ at 1 m s^{-1} ; 20 °C and 50% RH): this deviation could be explained by the effect of air velocity discussed further in this paper even if xylene SR is more in accordance with the one obtained before ($49.9 \pm 12.6 \text{ mL min}^{-1}$).

Detection limits, gathered in Table 2, are rationally lower for all VOC, using the thin diffusive body (between 0.01 and $0.51 \mu\text{g m}^{-3}$) than the thicker one (between 0.01 and $1.74 \mu\text{g m}^{-3}$). This is the reason why the thin diffusive body was initially preferred in this paper for short sampling time and so tested in laboratory experiments.

6.2. Meteorological parameter influence on the thin diffusive body 8 h-sampling rate

Table 3 gathers the results obtained from the fractional factorial design: for the eight experimental points, it gives the trial responses (that is to say the mean SRs of the 6 reproducible VOC on

Table 2

Standard sampling rates (mL min^{-1}), blank values (ng), and detection limits for 8 h sampling ($\mu\text{g m}^{-3}$) using thin and thick diffusive bodies.

	Thin body mean SR (n=8) \pm SD	Thick body mean SR (n=8) \pm SD	Thick body Radiello [®] SR \pm 2SD	Average blank value (n=6) \pm SD (ng)	DL thin body	DL thick body
IsP	173 ± 22	86 ± 11	–	–	0.01	0.01
THF	58 ± 7	35 ± 10	–	–	0.02	0.03
CyH	69 ± 3	30 ± 5	28 ± 15	3.9 ± 0.7	0.06	0.15
Tol	74 ± 4	31 ± 8	30 ± 8	5.2 ± 0.9	0.08	0.18
pXy	39 ± 7	16 ± 7	23 ± 11	4.7 ± 0.9	0.14	0.35
nDe	15 ± 3	4.3 ± 1.8	22 ± 22	3.5 ± 1.2	0.51	1.7

n: number of blank values; SR: sampling rate; SD: standard deviation.

IsP (Isopentane), THF (Tetrahydrofuran), CyH (Cyclohexane), Tol (Toluene), pXy (p-xylene), nDe (n-decane)

8 Radiello[®] samplers) and their corresponding factor values, and also the factor effect (FE) defined for each factor and each compound as the half-difference between the mean SR calculated from the "low conditions", and those calculated from the "high conditions".

Among the three factors, air velocity is the most influential with a significant positive FE for all compounds except for THF. Temperature also shows significant positive or negative FE (depending on the compound) but always lower than those relative to air velocity factor. Regarding humidity, FE is not significant for any compounds. This result is in good agreement with the hydrophobic properties of the adsorbent [40].

An air velocity increase leads to a SR increase of 6 and 37% per m s^{-1} depending on the VOC and considering a linear dependence between 2 and 7 m s^{-1} . A temperature increase leads to a decrease in the SR for Isopentane, Tetrahydrofuran and Cyclohexane of 1.0–2.4% per degree between 10 and 25 °C. Besides, temperature has no significant influence on the SR of toluene, p-xylene and n-decane. This result is unexpected since literature [40] reveal for BTEX a significant positive or negative effect of temperature on thick body SR. Fig. 1a proposed illustrates this discussion, gathering SR variation of VOC compared to the one obtained under conditions close to standard ones. The significant influence of air velocity on SRs highlighted by this experimental design calls into question the suitability of thin diffusive body when wind speed reaches high value.

6.3. Meteorological parameter influence on the thick diffusive body 8 h-sampling rate

Since thin diffusive body is not suitable for outdoor field VOC passive sampling under wind conditions upper to 2 m s^{-1} , the influence of wind velocity and temperature on the SR using a thick diffusive body was investigated. SRs calculated for the 6 VOC under the various conditions detailed in the methodology section are presented in Table 4. Fig. 1b compares the mean SRs obtained, for several conditions in the exposure chamber with ones given by Radiello furnisher, to the one obtained under standard conditions (25 °C, 50% HR, 2 m s^{-1}).

Using the thick diffusive body, the influence of air velocity on SR persists. An air velocity increase leads to a SR increase which varies with VOC between 12 and 32% per m s^{-1} considering a linear dependence between 2 and 7 m s^{-1} , even though the observed effect is more pronounced over 4 m s^{-1} . On the contrary, an air velocity change between 0.5 and 2 m s^{-1} seems to have no influence on SR. A multiple range test (Duncan) permits to confirm this idea: the 0.5– 2 m s^{-1} SR are not statistically different whereas a statistical difference (except for THF) exists between these 3 values and the

Table 3
Design of experiments of 8 conditions with two levels – mean sampling rates for thin diffusive body (mL min^{-1}) and relative standard deviation ($n=8$) – factor effects (in mL min^{-1}).

FFD levels			Weather conditions			IsP	THF	CyH	Tol	pXy	nDe
T	H	Av	T	H	AV						
Hi	Hi	Lo	25 ± 0.5	6.5 ± 0.1	2 ± 0.2	173 ± 22	58 ± 7	68 ± 3	74 ± 3	38 ± 7	14 ± 3
Hi	Hi	Hi	25 ± 0.5	6.5 ± 0.1	7 ± 0.2	258 ± 55	62 ± 13	130 ± 13	166 ± 17	130 ± 19	86 ± 18
Hi	Lo	Lo	25 ± 0.5	2 ± 0.1	2 ± 0.2	181 ± 24	73 ± 14	73 ± 6	79 ± 7	50 ± 9	28 ± 7
Hi	Lo	Hi	25 ± 0.5	2 ± 0.1	7 ± 0.2	269 ± 55	77 ± 19	130 ± 14	160 ± 15	118 ± 19	76 ± 20
Lo	Hi	Lo	10 ± 0.5	6.5 ± 0.1	2 ± 0.1	210 ± 30	98 ± 22	81 ± 5	86 ± 8	44 ± 12	18 ± 7
Lo	Hi	Hi	10 ± 0.5	6.5 ± 0.1	7 ± 0.2	311 ± 86	130 ± 45	135 ± 12	158 ± 7	108 ± 17	62 ± 30
Lo	Lo	Lo	10 ± 0.5	2 ± 0.1	2 ± 0.2	232 ± 11	114 ± 12	86 ± 4	89 ± 7	52 ± 14	24 ± 9
Lo	Lo	Hi	10 ± 0.5	2 ± 0.1	7 ± 0.2	361 ± 50	147 ± 29	144 ± 23	153 ± 14	111 ± 17	70 ± 17
Temperature effect						-29*	-27*	-5.6*	-0.8	2.7	3.7
Humidity effect						-11	-7.9	-2.3	0.2	-1.2	-2.1
Air velocity effect						50*	9.1	29*	39*	35*	26*

IsP (Isopentane), THF (Tetrahydrofurane), CyH (Cyclohexane), Tol (Toluene), pXy (p-xylene), nDe (n-decane)
Hi: High; Lo: Low; T: temperature ($^{\circ}\text{C}$), H: absolute humidity (g of water m^{-3}), AV: air velocity (m s^{-1})

* Significant factor effect.

7 m s^{-1} SR. The statistical difference between the 4 m s^{-1} SR and the $0.5\text{--}1\text{--}2 \text{ m s}^{-1}$ SR is nevertheless not observed for all compounds. Then, the temperature influence is not observed significantly in the range from 5 to 25°C except for n-decane.

Taking into account these results, air velocity and temperature cannot be so considered as non-significant parameters for VOC

concentration determination by Radiello[®] passive sampling. If a temperature correction can be considered, and SRs adjusted versus the average temperature, contribution of air velocity is more difficult to take into account. In fact, in landfills and more generally for outdoor conditions, wind velocity varies greatly with the topography of the area of interest and a mean air velocity should be

Hi: High ; Lo: Low ; T: temperature ($^{\circ}\text{C}$), H: absolute humidity (g of water.m^{-3}), AV: air velocity (m.s^{-1})

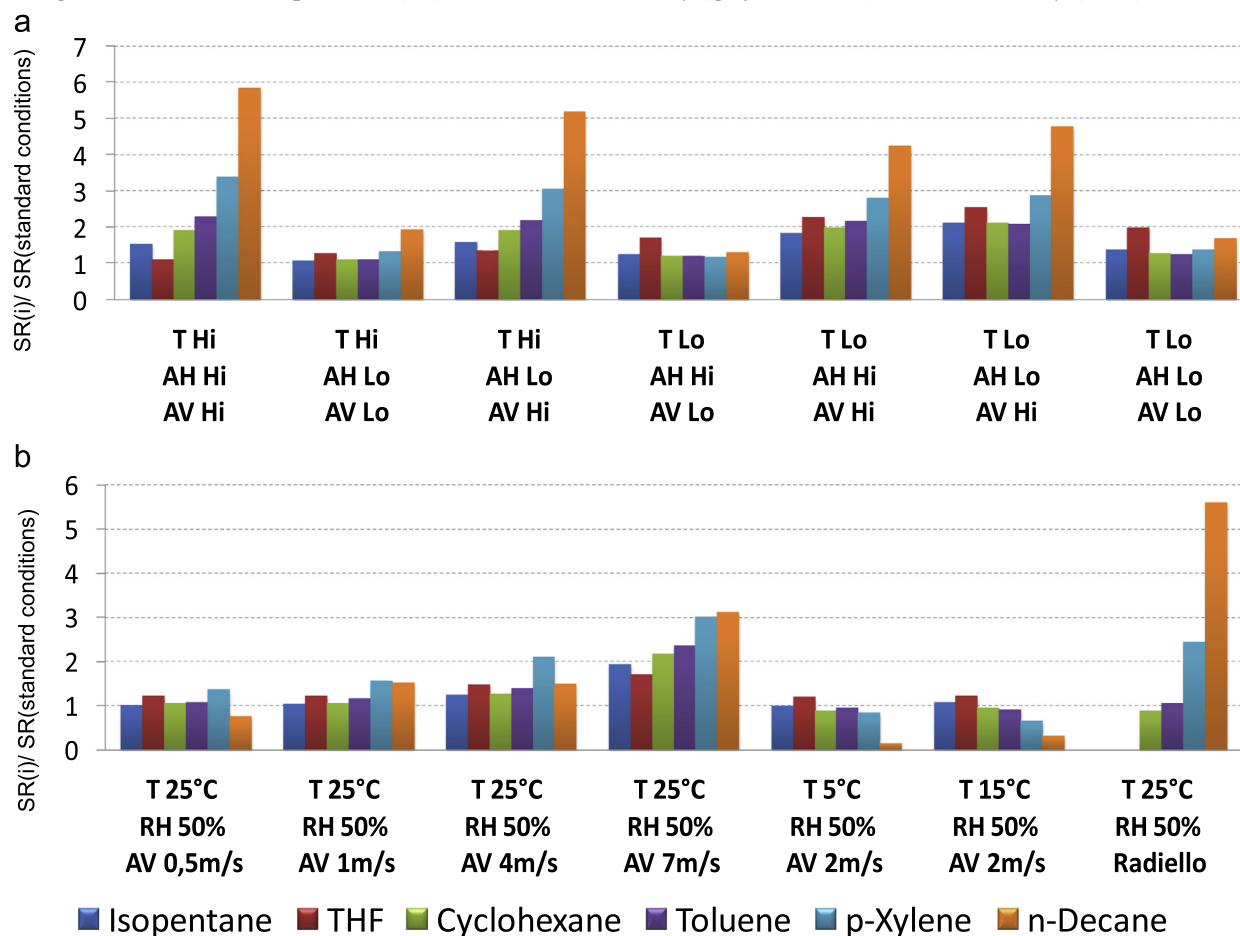


Fig. 1. Sampling rate variations at several weather conditions relatively to a sampling rate determined: under closer standard conditions (25°C , 30% HR, 2 m s^{-1}) for the thin diffusive body (a) and under standard conditions (25°C , 50%, 2 m s^{-1}) for the thick diffusive body (b). Hi: High; Lo: Low; T: temperature ($^{\circ}\text{C}$), H: absolute humidity (g of water m^{-3}), AV: air velocity (m s^{-1}).

Table 4Mean sampling rates for thick diffusive body (mL min^{-1}) and standard deviation ($n=8$).

Weather conditions			IsP	THF	CyH	Tol	pXy	nDe
T	H	AV						
25 ± 0.5	50 ± 5	0.5 ± 0.1	91 ± 13	40 ± 10	33 ± 3	31 ± 6	15 ± 7	3 ± 2
25 ± 0.5	50 ± 5	1 ± 0.1	93 ± 10	40 ± 7	33 ± 4	33 ± 4	17 ± 5	6 ± 3
25 ± 0.5	50 ± 5	2 ± 0.1	92 ± 1	33 ± 18	32 ± 1	29 ± 5	11 ± 5	4 ± 1
25 ± 0.5	50 ± 5	4 ± 0.1	112 ± 7	48 ± 6	40 ± 4	40 ± 5	23 ± 9	6 ± 2
25 ± 0.5	50 ± 5	7 ± 0.1	177 ± 26	56 ± 24	69 ± 13	68 ± 14	33 ± 16	12 ± 7
5 ± 0.5	50 ± 5	2 ± 0.1	90 ± 15	39 ± 6	28 ± 3	27 ± 2	9 ± 3	0.5 ± 0.4
15 ± 0.5	50 ± 5	2 ± 0.1	98 ± 10	40 ± 16	30 ± 5	26 ± 7	7 ± 6	1 ± 1

IsP (Isopentane), THF (Tetrahydrofurane), CyH(Cyclohexane), Tol (Toluene), pXy (p-xylene), nDe (n-decane)

T: temperature ($^{\circ}\text{C}$), H: relative humidity (%), AV: air velocity (m s^{-1})

required at each sample point. A wind tranquillization box designed by the manufacturer, could reduce wind velocity influence on SR in that the case of no wind direction change during the sampling duration. The best way to consider wind effect is to evaluate the uncertainty linked to SR changes.

6.4. Uncertainty estimation

Considering the air velocity influence and the difficulty to accurately estimate the SR, an estimation of the ambient concentration uncertainties is needed for a reliable use of the Radiello[®] sampler. The purpose of this section is to associate an uncertainty value to each measured VOC concentration. As a first step and according to Eq. (1), uncertainty sources have been distributed between sampling mass, sampling time and SR.

According to the guideline for measurement of uncertainty (NF ENV 13,005) [41], uncertainty $u(C)$ can be obtained from Eq. (1):

$$u^2(C) = \left(\frac{1}{t \cdot \text{SR}}\right)^2 * u^2(m - m_b) + \left(\frac{m - m_b}{t \cdot \text{SR}^2}\right)^2 * u^2(\text{SR}) + \left(\frac{m - m_b}{t^2 \cdot \text{SR}}\right)^2 * u^2(t) \quad (2)$$

where $u(m - m_b)$ represents the uncertainty linked to the detected and the blank masses, $u(\zeta)$ the uncertainty linked to the recovery rate, $u(\text{SR})$ the uncertainty on SR and $u(t)$ the uncertainty due to sampling time.

The uncertainty $u(m - m_b)$ can be expressed by Eq. (3)

$$u^2(m - m_b) = \left(\frac{1}{k}\right)^2 * u^2(A) + \left(\frac{1}{k}\right)^2 * u^2(A_b) + \left(\frac{A - A_b}{k^2}\right)^2 * u^2(k) \quad (3)$$

where $(m - m_b) = \frac{(A - A_b)}{k}$

This uncertainty $u(m - m_b)$, is linked to

1. the analytical reproducibility expressed by $u(A)$, calculated as the RSD of seven standard tubes spiked with about 100 ng of each compounds;
2. the uncertainty of blank masses $u(A_b)$, estimated from the dispersion of ten non-exposed tubes (conditioned and analyzed in the same conditions as exposed one);
3. the uncertainty on the coefficient response estimated from the difference between the mass of compounds calculated from the regression curve equation and the mass of compounds in the calibration standards (about 100 ng);

and the uncertainty of standard calibration masses.

The uncertainty of sampling time $u(t)$ corresponds to the time for positioning and removing the sampling tube which is estimated to 5 min for a 8 h sampling.

The uncertainty corresponding to the SR, $u(\text{SR})$ can be estimated using two methods:

1. the SR depending on the air velocity is estimated by a regression curve established between 2 and 7 m s^{-1} from which derives the uncertainty;
2. a reference SR is defined (25 $^{\circ}\text{C}$, 50%HR, 2 m s^{-1}) and the uncertainty is calculated from the difference between SRs measured at 0.5 and 2 m s^{-1} in a first step and then at 2 and 7 m s^{-1} .

Fig. 2 gathers the estimation of the relative uncertainties on the concentration of the 6 compounds of interest and the contribution of each source to the global uncertainty using the two methods of $u(\text{SR})$ calculation.

Relative uncertainty values vary between 4 and 12% for the 6 VOC using the reference SR, and considering only the variation of SR between 0.5 and 2 m s^{-1} (as usually reported in literature [42]). In this case, uncertainty linked to SR estimation is quite low, and mass uncertainty mainly contributes to global uncertainty. But if we consider the high SR variation between 2 and 7 m s^{-1} , a very significant increase of the uncertainty until 55% for decane is noticed, and SR uncertainty is now the main contributor. SR can also be estimated as a function of air velocity. A linear regression has been used between SR and air velocity varying from 2 to 7 m s^{-1} ; and good fit, with R^2 up to 0.85 was obtained, except for xylene which exhibits a R^2 of 0.75 due to highly dispersed results. The use of a modeled SR allows a new estimation of uncertainty (which include the R^2 value), and contributes to significantly reduce it, except for xylene. Uncertainties are so comprised between 13 and 36%. In spite of this, SR uncertainty remains the main contribution to global uncertainty.

Concentration uncertainty was estimated by Pennequin-Cardinal et al. [40] for the BTEX using Radiello[®] samplers for an exposure time of 7 days, and taking into account an air velocity dependence between 0.1 and 3 m s^{-1} . The reported extended relative concentration uncertainties ($2u^2C/C$) are respectively 19 and 31% for toluene and p-xylene which are comparably little bit higher with results (4% and 10% for toluene and p-xylene – non-extended uncertainty respectively) when air velocity effect over 2 m s^{-1} is neglected.

7. Discussion

The literature already reports works focused on meteorological conditions and sampling time influence [27,40,43] but rarely on short sampling duration (mainly on days), concerning these compounds (mainly on BTEX) of interest and on a large range of air velocities. This work is the only study which focuses on over 3 m s^{-1} air velocity effects, whereas local wind velocity can frequently reach such a value. Surprisingly, the relative (to standard conditions) influence of air velocity variation is in the same order

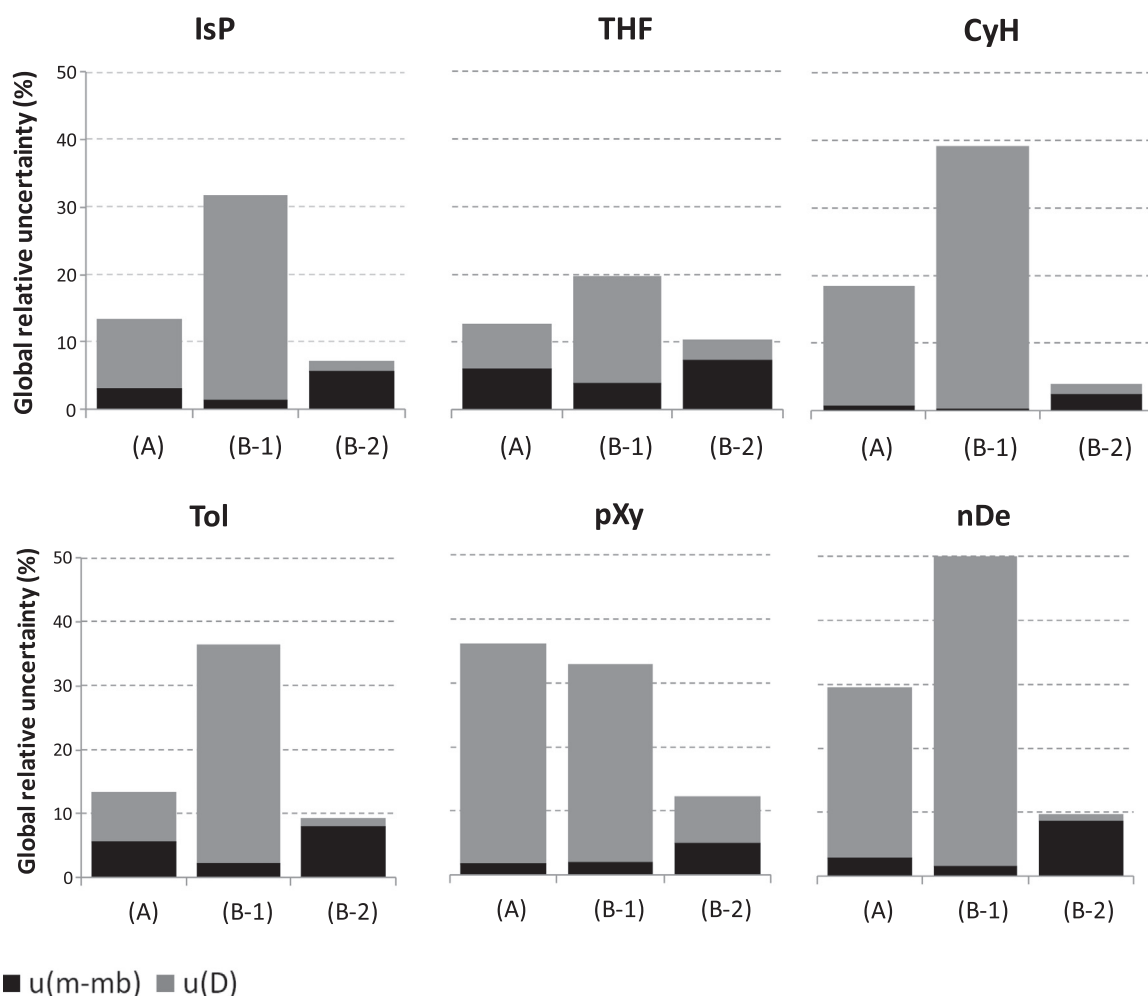


Fig. 2. Global relative uncertainties for VOC measurements by Radiello[®] sampling ($u(C)/C$) (%) due to sampled mass ($u(m-mb)$), sampling time ($u(t)$), and sampling rates ($u(D)$) uncertainties. IsP (Isopentane), THF (Tetrahydrofuran), CyH (Cyclohexane), Tol (Toluene), pXy (p-xylene), nDe (n-decane). (A) Uncertainty estimated if SR is modeled between 2 and 7 $m s^{-1}$. (B-1) Uncertainty estimated if a standard SR is considered and taking into account the SR variability due to wind speed comprised between 2 and 7 $m s^{-1}$. (B-2) Uncertainty estimated if a standard SR is considered and taking into account the SR variability due to wind speed comprised between 0.5 and 2 $m s^{-1}$. $u(t)$ is always < 1%.

of magnitude for the thick diffusive body than for the thin one. A quite limited effect of about 30% is observed between 2 and 4 $m s^{-1}$ but SRs increased to more than 100% for the majority of target compounds between 4 and 7 $m s^{-1}$. Thick body samplers SR are announced as invariant with wind speed between 0.1 and 10 $m s^{-1}$ by the Radiello[®] manufacturer, and this information is relayed in a practical consideration section by Gallego et al. [39]. Conversely, the absence of air velocity effect is confirmed between 0.1 and 1.3 $m s^{-1}$ for BTEX by Mason et al. [27] but we observed in previous works (Pennequin-Cardinal et al. [40]) an air velocity influence from 0.1 to 3 $m s^{-1}$: an increase of 15–20% in the SR is then detected for BTEX. Our present results show that from 0.5 $m s^{-1}$ to 2 $m s^{-1}$, the SR increase for toluene and p-xylene is respectively 17 and 38%, which is in accordance with our previous results [38] taking into account the results dispersion. Some additional measurements have been performed on the thick diffusive body in order to characterize its air resistivity. A porosity of 44.8% with a mean pore size of 39 μm has been measured thanks to the mercury porosimetry technique [44] whereas Radiello[®] furnisher announces a pore size of 10 μm . It confers a permeability of $1.3 \times 10^{-11} m^2$ against $2.0 \times 10^{-10} m^2$ obtained from our data: that is to say, that the thick diffusive body is 10 times less air resistant than it is announced. To go further, Reynolds number was determined considering pore hydraulic diameter as the characteristic dimension. Taking into account the porous parameters obtained with mercury porosimetry, Reynolds number calculated for an air

velocity of 2.5 $m s^{-1}$, is not representative of a linear laminar flow but is representative of an air flow influenced by inertial effects [45]; which is quite consistent with our observations.

Regarding temperature influence, Radiello[®] manufacturer validates that SR varies with temperature and proposes a mathematical relation to estimate thick body SR. This variation is estimated to be $\pm 5\%$ for 10 $^{\circ}C$ variation. We previously have identified different effects of temperature increase on SR according to the compounds leading to a decrease for the benzene and an increase for the aromatic compounds (Pennequin-Cardinal et al. [40]). The results from this previous work are in good accordance with this study. For heaviest compounds (toluene, xylene and decane) an increase is observed; the variation is as much significant as the SR is low. For cyclohexane, a same behaviour as benzene is observed. No significant effect is noticed for isopentane and THF.

8. Application to atmospheric samples

8.1. Measurement in the atmosphere of a landfill site

Considering that the objective of this work was to assess the feasibility of passive-VOC-8 h-measurements on landfill taken into account high fluctuating meteorological conditions, only a day of field measurement is shown here as an example of application. The Radiello[®] device equipped with the thick body has been used,

Table 5

Mean VOC concentrations ($\mu\text{g m}^{-3}$) determined using the standard SR ($25\text{ }^{\circ}\text{C}-50\text{ HR}-2\text{ m/s}$) and concentration dispersion amongst sample points measured in May 2013 for three landfills area (see samplers position in Supplementary information section).

	Upwind site (n=2)		Site on exploitation (n=3)		Downwind site (n=4)		Uncertainty*
Isopentane	2.79	± 1.85	3.31	± 1.13	2.73	± 3.13	31%
Pentane	0.28	± 0.30	0.60	± 0.10	0.77	± 1.25	
2-me-pentane	0.20	± 0.20	0.27	± 0.12	0.17	± 0.21	
Benzene	2.37	$\pm \pm 0.04$	2.16	± 0.71	2.34	± 0.96	35%
Toluene	0.48	± 0.04	0.78	± 0.04	0.81	± 0.41	
Ethylbenzene	< LD		0.12	± 0.06	0.35	± 0.48	
m,p-Xylene	0.52	± 0.08	0.95	± 0.45	1.48	± 1.58	32%
Tetrahydrofurane	< LD		< LD		< LD		
Cyclohexane	< LD		< LD		< LD		
Decane	< LD		< LD		< LD		

Sampling rate estimation: SR pentane=SR isopentane; SR 2-me-pentane=SR cyclohexane, SR benzene=SR benzene Radiello, SR ethylbenzene=SR ethylbenzene Radiello.

* Uncertainties have been determined following the estimation procedure described in Section 4 using a reference SR and taking into account the variability due to wind speed over 2 m s^{-1} .

on nine sampling locations, for 8 h. Targeted VOC, but also other light alkanes and aromatics associated to their uncertainty values were determined for each position. Table 5 gathers VOC concentrations and RSD value which represent the concentration distribution between the different samplers located in the same part on the site (upwind position, on-site position and downwind position). Among the targeted VOC, isopentane and benzene are the two major compounds, with concentration levels around $2\text{ }\mu\text{g m}^{-3}$. Pentane, 2-methylpentane, toluene, ethylbenzene and xylene were measured in average at a concentration below $1\text{ }\mu\text{g m}^{-3}$. Finally, THF, cyclohexane and decane concentrations were below the detection limit. These observed concentrations are quite low compared to those reported by the literature [3,6–8], which report sometimes more than ten times higher VOC levels (Table 1).

Ethylbenzene, toluene and p-xylene concentrations measured close to the site of 'Séché Environnement' seem to be in the low range of concentrations usually measured in similar other sites. It could be explained by the very low permeability of coverage layer and the high performance of the biogas collection network. If we look at the concentration ratio between upwind and downwind sampling points, the landfill site seems to appear as a significant source of pentane, ethylbenzene, xylene and even less so, toluene; but it is not the case for isopentane and benzene suggesting that the landfill is not the main source of these compounds. Nevertheless the relatively high concentration of benzene comparatively to toluene could exhibit a local source which could be associated with biomass burning emissions. Taken into account the few number of measurements, conclusions have to be confirmed by replicate measurements in the same periods but also in different seasons. Other field campaigns will be conducted, and further papers will present the daily and seasonal concentration variability.

9. Conclusion

In this work, the radial diffusive sampler filled with Carbograph 4 was evaluated for monitoring VOC from biogas. It has been shown for 6 targeted compounds that: (i) SR does not depend on air velocity below 2 m s^{-1} as announced by the furnisher, (ii) but when air velocity is over 2 m s^{-1} a great influence on VOC's SR is noticed regardless of the type of diffusive body used, (iii) temperature has a limited influence (compared to wind influence), which is estimated to less than 3% per degree, and highly dependent of the considered compound; (iv) humidity has no influence on the SR of VOC. Uncertainty sources for VOC concentrations by Radiello samplers are listed: (i) sampling mass, (ii) sampling time

and (iii) SR. Relative uncertainty values depend on VOC and change in the range of 18–54%. For all compounds the SR uncertainty is the main contributor.

These current laboratory tests confirm that converging towards passive measurements in a sampling strategy implies to accept a large uncertainty on concentrations due to significant influence of meteorological parameters. Choosing the Radiello® passive sampler to assess the ambient VOC concentrations in landfill surroundings, must be done keeping in mind that not all of the VOC biogas would be measured with a "reasonable" uncertainty inferior to 50% (depending on wind condition variability). In fact, Carbograph 4 is not a universal sorbent for VOC as diversified; and moreover conditions chosen for the GC analysis reach a compromise in order to suit with the largest VOC range.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.talanta.2015.05.083>.

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