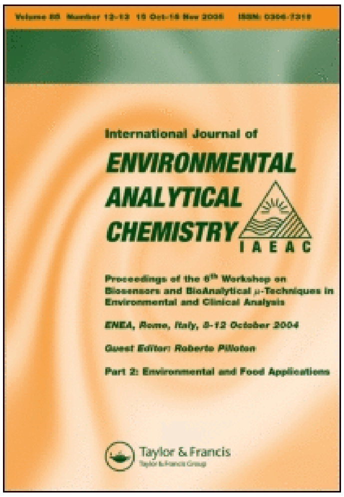

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Characterisation and On-Site Monitoring of Odorous Organic Compounds in the Environment of a Landfill Site

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CHARACTERISATION AND ON-SITE MONITORING OF ODOROUS ORGANIC COMPOUNDS IN THE ENVIRONMENT OF A LANDFILL SITE

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This study presents an analytical procedure developed in order to monitor specific volatile organic compounds (VOC) causing olfactive nuisances in the environment of a landfill site. 1-Methyl-4-*iso*-propenyl-1-cyclohexene (limonene) and 1-methyl-4-*iso*-propyl-benzene (*p*-cymene) detected by GC-MS in the landfill gas emissions were considered as tracers of the malodour. An on-line analytical system including a gas chromatograph coupled with a photoionisation detector was installed "on-site" to detect these markers at $\mu g/m^3$ level in the atmosphere after pumping up the ambient air at close intervals. Quantitative results of the semi-continuous monitoring were strongly correlated with olfactive nuisances reported in the vicinity of the source. The chemical characterisation of odorous organic tracers and their "on-site" monitoring was shown to be a useful technique to detect malfunctions in the bio-gas collecting facilities and to prevent air pollution and olfactive nuisances in the environment.

Keywords: Landfill site; volatile organic compounds (VOC); olfactive nuisances; on-site detection; gas chromatography; limonene; *p*-cymene

INTRODUCTION

Anaerobic digestion of municipal wastes discharged in landfill sites produce Volatile Organic Compounds (VOC) which can cause olfactive nuisances in the environment. Although collecting techniques have been developed to burn the gaseous emissions at flares and/or to use it as combustible for diesel motors, their

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control in a closed circuit is not completely efficient. As a consequence, a fraction of odorous VOC is released to the atmosphere causing discomfort to local residents.

This paper describes a procedure developed to semi-continuously monitor characteristic odorous volatile compounds released from the dump. The objectives of the study was to evaluate the management system used to eliminate the landfill gas and to estimate the impact on surrounding population by means of on-site monitoring.

Whatever the quantity of waste and its composition, the global landfill gas emissions are generated by two different sources named «bio-gas» and «fresh waste emissions ». The first one consists of emitted gas leaking from the collecting network facilities or from free, uncollected emissions. Gaseous emissions released by the most recent waste on the discharging and handling site are usually named « fresh waste emissions ».

Only a few volatile organic compounds detected by Gas Chromatography-Mass Spectrometry (GC-MS) can be considered as markers of the malodour. Indeed, the anthropic activity (truck exhaust gases for instance), which is strongly present on the site and in the direct environment of the landfill site, produces volatile compounds which interfere with the measurements.

1-Methyl-4-*iso*-propenyl-1-cyclohexene (limonene) and 1-methyl-4-*iso*-propyl-benzene (*p*-cymene), which contribute to the global municipal waste olfactory sensation, can be used as odour markers in order to semi-continuously monitor bad odours by means of a cold trapping gas analyser. These compounds are released by the biodegradation of vegetable matter. More specifically, *p*-cymene is considered as a bio-gas tracer, while limonene is a « fresh waste emissions » indicator.

After the GC-MS characterisation of the tracers, a semi-continuous monitoring system consisting in a gas chromatograph equipped with a photoionisation detector was installed on-site. Quantitative results of analyses performed with direct sampling of ambient air are reported and illustrated by showing the evolution of limonene and *p*-cymene concentration in function of time. Strong positive correlation are observed between the quantitative monitoring of the tracers concentration and the general olfactory perception in the environment.

The monitoring of organic tracers appears to be a useful technique to detect problems and an efficient tool to assist the management of the site by forecasting air pollution episodes.

EXPERIMENTAL

Methodology

Both « bio-gas » and « fresh waste emissions » were analysed by GC-MS. After the characterisation of tracers from each origin, a semi-continuous monitoring system consisting of a gas chromatograph equiped with a photoionisation detector (PID) was installed on-site. The monitor was installed in a dedicated conditioned container located on the edge of the landfill site 4 meter height above ground level.

GC-MS landfill gas analyses

Sampling

The « bio-gas » was sampled at a flare by means of 15 dm^3 Tedlar bags by overpressure. Sampling ambient air on the discharging and handling site was performed by pumping 20 dm^3 (1 dm^3/min) through a Tenax® TA / carbotrap adsorbent trap. Sampling was performed at 1.5 meter height.

Material and methodology

Characterisation of VOC present in the gaseous emissions was carried out using enrichment and thermal desorption GC-MS. 5 cm^3 are taken from the sampling bags and concentrated on a Tenax® TA adsorbent at room temperature. VOC adsorbed on the cartridge are analysed by GC-MS after thermal desorption at 240°C in a stream of helium. The Tenax® TA / carbotrap adsorbent traps, were directly placed in front of the GC system and thermal desorbed at 240°C.

The analytical system configuration consists of a Tekmar LSC 2000 thermal desorber directly coupled by means of a heated fused silica transfer line to a gas chromatograph (CE Instruments GC 8000) coupled with a quadrupole mass spectrometer (Fisons MD 800). A capillary cryofocussing unit (CE Instruments MFA 815) using liquid nitrogen is used to focus the volatiles at the narrow bore column head.

Chromatography

The separation column (DB 502 60m × 30m × 1.8μm) was obtained from J&W Scientific (Folsom, USA). After thermal desorption at 240 °C, the oven temperature was programmed from 35°C to 245°C at 5°C/min. Helium was used as carrier gas at a constant pressure of 120 kPa.

Mass spectrometric detection and quantification

Detection was performed in full scan electron impact mode with a total cyclus of 0.5 sec. Masses with m/z from 29 to 300 Th were scanned in 0.4 sec.

Compounds detected and reported in Tables I and II are semi-quantitatively analysed using internal or external standard method according to the type of sampling.

On-site monitoring

Generally speaking, the choice for a specific analytical system (and the selection of a detector in particular) is the result of a complex compromise between financial constraints and technical requirements like sensitivity and selectivity. This is particularly true when on-site field monitoring is required in an industrial environment.

Material

The analytical system (Trace Gas Analyser ^{tm}) developed by CE Instruments [1] was used to determine and quantify trace gases in air *in situ*. It consists of a concentrating unit and a gas chromatograph coupled with a PID detector (PID 80).

The main advantage of the system is that it uses only compressed air for cooling the concentration unit and helium as a single gas supply for the carrier, the detector make-up and detector cooling. The schematic diagram of the instruments is shown in Figure 1.

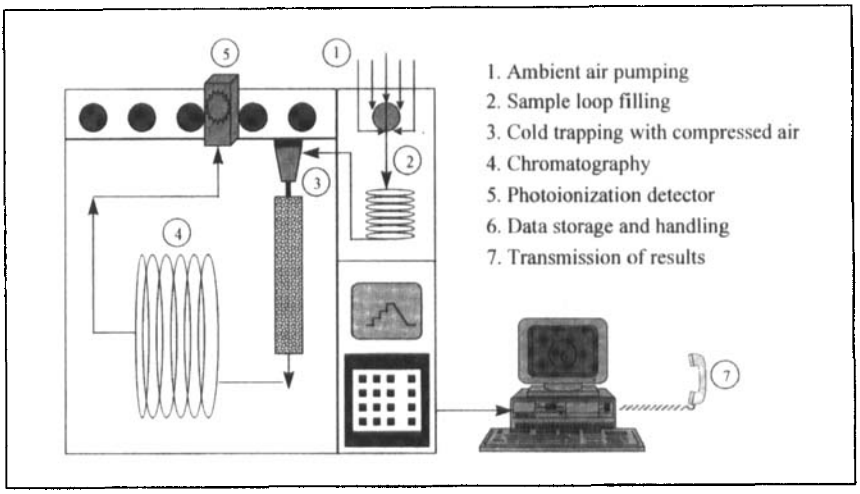

FIGURE 1 On-site monitoring of VOC by means of the Trace Gas Analyser^{TM}: Schematic diagram. See "On-site monitoring material" in text for further details

The system fully automatically performs all the steps needed for the analyses including ambient air pumping, sample loop filling, cold trapping, transfer into the chromatographic column, and finally chromatographic analysis. The trapping system is based on a 0.7 mm external diameter fused silica microtrap containing 6 cm of Tenax® GR 35–60 mesh adsorbent material. It is cooled with compressed air to a temperature of 35°C.

Sampling, chromatography and detection

Every two hours, during day- and nighttime, 100 ml of ambient air were pumped up, cold trapped and transferred at 50 ml/min into the separation column after a thermal desorption at 240°C controlled by the MFA unit. The separation column (methyl polysiloxane 60m × 0.32mm × 1μm) was purchased from J&W Scientific (Folsom, USA). After the transfert, the oven temperature was programmed from 47°C to 220°C at 5°C/min. Helium was used as carrier gas at a constant pressure of 120 kPa. The detection system was a PID which produced UV radiation at 10.2 eV and maintained at 250°C to avoid condensation and clouding of the PID window. To achieve quantification of limonene and *p*-cymene, the instrument was calibrated by pumping 100 ml from new Tedlar bags containing four known amounts of each standard. The concentration of these compounds was calculated by comparison to their calibration curve fitted using linear regression and the on-line analytical system was checked for leaks of limonene and *p*-cymene by controlling at close intervals the response factors of known amounts of standards.

Sniffing

At the same time and at the same place where the samplings were performed, the odours were perceived by some persons who reported the intensity of the smell. Malodour intensity values varied from 1 to 4 meaning respectively: "absence of odour", "weak odour", "moderately nauseous" and "foul".

Products

Limonene and *p*-cymene (>99%) used for calibration were purchased from Aldrich. Helium (N60) from Air Liquide.

RESULTS

GC-MS landfill gas analyses

Results for the semi-quantitative GC-MS analyses are reported in Table I (for the bio-gas) and in Table II (for the « fresh waste emissions »).

TABLE I GC-MS analysis for the bio-gas Compounds are quantitatively analysed using internal standard method

Compounds	*Concentration mg/Nm^3*
1,2-*cis*-Dichloroethylene	0,2±0,03
1,2,3-Trimethylbenzene	1,3±0,13
1,2,4 -Trimethylbenzene	9,5±0,95
1,3,5-Trimethylbenzene	4,7±0.47
1-methyl hexene	0,90±0,14
1-Propanol	0,2±0,04
2-Butanol	0,89±0,18
2-Butanone	1,2±0,17
2-methyl hexane	1,2±0,18
2-methyl pentane	0,63±0,13
2-Pentanone, 4-methyl	0,7±0,08
3-methyl hexane	1,8±0,26
3-methyl pentane	0,42±0,08
a-Pinene	74±11
Alkane C8	0,2±0,03
Alkane C8	0,6±0,09
Alkane C8	0,74±0,11
Alkane C8	0,91±0,14
Alkane C8	1,8±0,27
Alkane C9	0,6+0,07
Alkane C9	1,2±0,19
Alkane C9	1,5±0,15
Alkane C9	2,1±0,32
Alkane C9	5,8±0,87
Alkane C9	6,6±0,70
Alkane C10	0,77±0,12
Alkane C10	10±1,6
Alkane C10	18±2,8
Alkane C10	2,0±0,20
Alkane C10	2,4±0,37
Alkane C10	3,0±0,30

Compounds	*Concentration mg/Nm*^{3}
Alkane C10	9,1±1,4
Alkane C10	9,1±1,4
Alkane C10	9,3±0,93
Alkane C11	0.70±0.11
Alkane C11	0,70±0,11
Alkane C11	1,4±0,21
Alkane C11	1,9±0,29
Alkane C11	2,6±0,39
Alkane C11	6,8±1,0
b-Pinene	7,7±1,2
Benzene	0,6±0,03
Butyl acetate	0,4±0,04
Butyl cyclopentane	1,9±0,29
C4 Alkylbenzene	0,9±0,09
C4 Alkylbenzene	0,91±0,09
C4 Alkylbenzene	1,8±0,18
Chlorobenzene	0,3±0,03
Cyclchexane	0,88±0,13
Cycloalkane C10	3,9±0.59
Cycloalkane C10	1,6±0,24
Cycloalkane C11	2,2±0,33
Dichloromethane	0,5±0,06
Diisopropyl butyrate	0,2±0,02
Dimethyl cyclohexane	0,50±0,10
Dimethyl cyclohexane	2,0±0,30
Dimethyl cyclopentane	0,3±0,04
Dimethyl disulfide	0,1±0,02
Dimethyl furane	0,1±0,02
Dimethyl pentane	0,51±0,08
Dimethyl sulfide	0,05±0,02
Ethyl-dimethyl cyclohexane	0,4±0,06
Ethyl-methyl cyclohexane	0,68±0,10
Ethyl-methyl cyclohexane	3,3±0,50
Ethyl-methyl cyclohexane	4,2±0,62
Ethyl acetate	0,3±0,06
Ethyl butyrate	4,8±0,48
Ethyl cyclohexane	1,8±0,36
Ethyl hexanoate	0.6±0,07
Ethyl isobutyrate	0,86±0,13
Ethylbenzene	24±2,4

Compounds	*Concentration mg/Nm^3*
Ethyl propionate	0,66±0,10
Hydrogene sulfide	0,1±0,04
Isobutanol	0,1±0,05
Isopropylbenzene	1,3±0,13
Limonene	**68±6,9**
m- + p-Xylenes	33±3,3
m-Ethyltoluene	2,0±0,20
Methyl-propyl cyclohexane	0,65±0,10
Methyl butyrate	0,97±0,15
Methyl cyclohexane	2,7±0,41
Methyl cyclopentane	0,2±0,05
Methylstyrene	0,1±0,02
Monoterpenic hydrocarbon	6,2±0,93
n-Butanol	1,2±0,23
n-Decane	41±6,1
n-Dodecane	0,4±0,04
n-Heptane	3,5±0,36
n-Hexane	1,2±0,24
n-Nonane	33±3,3
n-Octane	5,4±0,54
n-Pentane	1,0±0,20
n-Propylbenzene	2,5±0,25
n-Undecane	6,1±0,61
Napthalene decahydro	0,90±0,14
o-Ethyltoluene	3,0±0,30
o-Xylene	7,9±0,80
p-Ethyltoluene	5,5±0,55
p-Cymene	**43±4,3**
Propyl acetate	0,3±0,04
Propyl butyrate	0,90±0,09
Propyl cyclohexane	4,6±0,68
Styrene	1,2±0,12
Tetrachloroethylene	4,8±0,48
Toluene	38±3,8
Trichloroethylene	0,7±0,07
Trimethyl cyclohexane	0,5±0,07
Trimethyl cyclohexane	2,3±0,34
Trimethyl cyclohexane	2,1±0,32
Trimethyl cyclopentane	0,2±0,04

TABLE II GC-MS analysis for the "fresh waste amissions" Compounds are quantitatively analysed using external standard method

Compounds	*Concentration mg/Nm^3*
1,1,1-Trichloroethane	0,05±0,01
1,2,4-Trimethylbenzene	0,1±0,01
1,3,5-Trimethylbenzene	0,02±0,01
6-methyl-5-Hepten-2-one	0,1±0,01
a-Pinene	0,2±0,03
Butyl acetate	0,2±0,02
Acetic acid	0,06±0,01
Alkane C10	0,09±0,02
Alkane C10	0,1±0,02
Alkane C10	0,1±0,02
Alkane C9	0,05±0,01
Alkane C9	0,07±0,01
Alkane C10	0,1±0,02
Alkane C11	0,09±0,02
Benzaldehyde	0,1±0,02
Benzene	0,06±0,01
Dichlorotetrafluoroethane	0,50±0,10
Phenyl ethanone	0,1±0,02
Ethylbenzene	1±0,1
Monoterpenic hydrocarbon	0,09±0,01
Monoterpenic hydrocarbon	0,1±0,02
Limonene	**7,9±1,2**
m- + p-Xylene	0,2±0,03
m-Ethyltoluene	0,01±0,01
n-Decane	0,5±0,07
n-Nonane	0,4±0,06
n-Propylbenzene	0,01±0,01
n-Undecane	0,2±0,03
o-Ethyltoluene	0,03±0,01
o-Xylene	0,06±0,01
p-Ethyltoluene	0,02±0,01
p-Cymene	**0,20±0,03**
Tetrachloroethylene	0,06±0,01
Toluene	0,4±0,04
Trichloroethylene	0,1±0,01
Trichlorofluoromethane	5,7±1,1

As illustrated in Table II, the global municipal waste olfactory sensation characterised on the working site of the dump under study is mainly due to monoterpenic hydrocarbons and to a lesser extend to monoaromatic hydrocarbons.

Table III reports the olfactory thresholds [2,3] and the measured concentrations for different compounds present in the bio-gas and in the « fresh waste emissions ». GC-MS analyses reveal the presence of VOC at concentrations higher than their perception threshold, indicating that leaks from the collecting network could cause olfactive nuisances.

TABLE III Olfactory thresholds and measured concentration for different compounds present in the "bio-gas" and in the "fresh waste emissions"

Compounds	*Olfactory treshold* mg/m^3	*References* (2), (3)	*Conc. in "bio-gas"* mg/Nm^3	*Conc. in "fresh waste emissions"* mg/Nm^3
Monoaromatic Hydrocarbons				
Benzene	2.5	Elfimova, 1966	0,6±0,03	0,06±0,01
Toluene	13.70	Köster, 1971	38±3,8	0,4±0,04
Ethylbenzene	0.40	Köster, 1971	24±2,4	1±0,1
m + p-Xylene	8.00	Köster, 1971	33±3,3	0,2±0,03
o-Xylene	11.00	Köster, 1971	7,9±0,80	0,06±0,01
Isopropylbenzene	0.03	Elfimova, 1966	1,3±0,13	Not detected
p-Cymene	0.01	Backman, 1917	43±4,3	0,20±0,03
1,3,5-Trimethylbenzene	0.20	Deadman, 1959	4,7±0,47	0,02±0,01
1,2,4 -Trimethylbenzene	0.70	Deadman, 1959	9,5±0,95	0,1±0,01
Alcohols				
n-Propanol	0.05	Summer, 1971	0,2±0,04	Not detected
n-Butanol	0.90	Laffort, 1973	1,2±0,23	Not detected
2-Butanol	9.00	Laffort, 1973	0,89±0,18	Not detected
Esters				
Ethyl acetate	27.00	Laffort, 1973	0,3±0,06	Not detected
Ethyl propionate	0.3–0. 5	Backman, 1917	0,66±0,10	Not detected
propyl acetate	0.1–0.5	Backman, 1917	0,3±0,04	Not detected
Butyl acetate	0.03	Hellman, 1974	0,4±0,04	0,2±0,02
Sulfides				
Hydrogene sulfide	0.0016	Lindvall, 1970	0,1±0,04	Not detected
Dimethyl sulfide	0.002–0.03	Lindvall, 1970	0,05±0,02	Not detected
Monoterpens				
a – Pinene	0.016	Appel, 1969	74±11	0,2±0,03
Limonene	0,01	Appel, 1969	68±6,9	7,9±1,2

In order to characterise landfill gas tracers, specific compounds released from the bio-gas and the « fresh waste emissions » were searched.

As an example, a full scan chromatogram obtained for the « fresh waste emissions» analysis is illustrated in Figure 2.

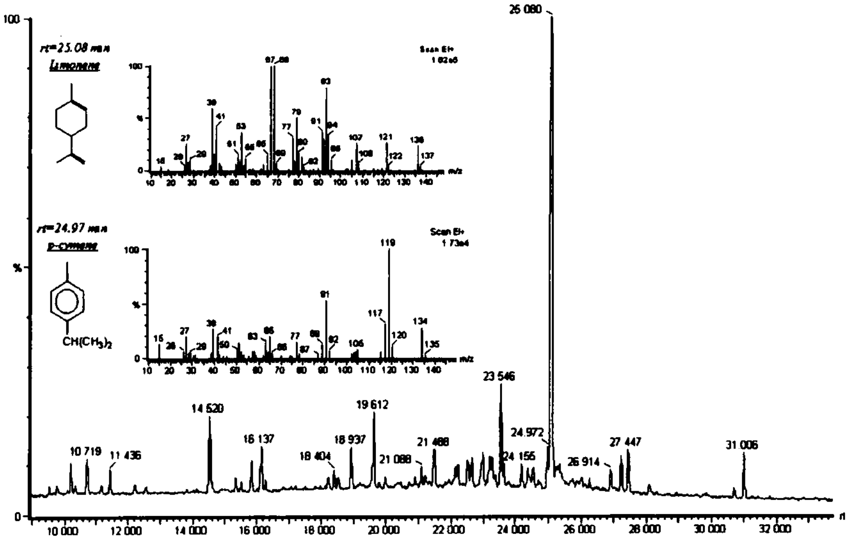

FIGURE 2 EI+ full scan GC/MS chromatogram obtained for the "fresh waste emissions" analysis. *p*-cymene and limonene are respectively detected at a retention time equal to 24.97 min and 25.08 min.

Analysis is performed on a DB 502 column with He as carrier gas at 120 kPa. Temperature is programmed from 35°C to 245°C at 5°C/min. Ions with m/z from 29 to 300 Th are scanned in 0.4 sec

As illustrated, limonene and *p*-cymene, were detected respectively at a retention time equal to 25.08 min. and 24.97 min. These compounds were selected as specific markers of the odours.

This choice was justified on the one hand by their considerable and selective contribution in the gaseous emissions released by the dump and on the other hand by the fact that they were easily detectable at the µg/m^3 level with a PID, requiring low investment and easy maintenance.

On site monitoring of limonene and *p*-cymene

A chromatogram, obtained for a landfill gas analysis performed on site is illustrated in Figure 3.

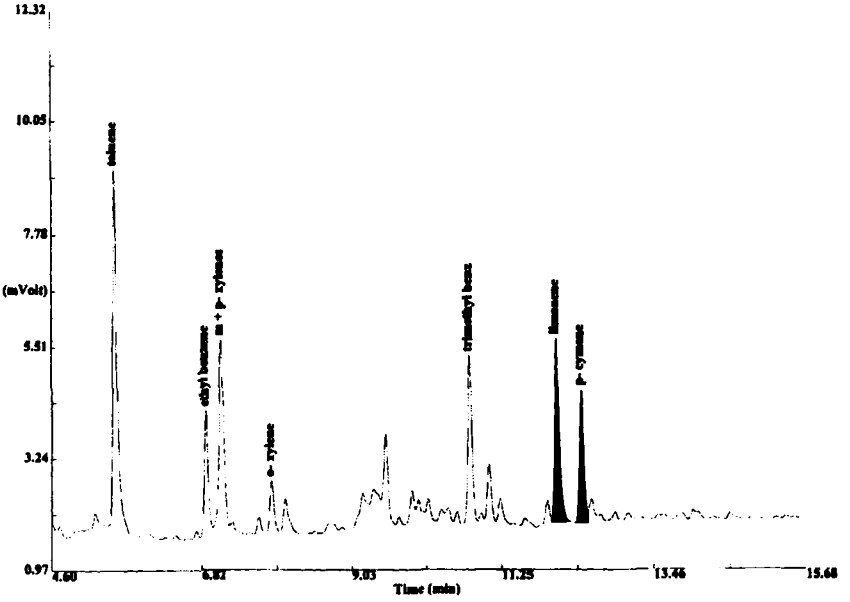

FIGURE 3 PID chromatogram obtained for a landfill gas analysis performed on site. Limonene and *p*-cymene are respectively detected at 12.05 min and 12.41 min. 100 ml of ambient air are analysed on a DB1 methyl polysiloxane column with He as carrier gas at 120 kPa. Temperature is programmed from 47°C to 220°C at 5°C/min. PID produces UV radiation at 10.2 eV

Major peaks have been identified by GC-MS (toluene at 5.53 min, ethyl-benzene at 6.88 min, *m*- + *p*-xylenes at 7.11 min, *o*-xylene at 7.85 min, trimethylbenzene at 10.78 min). Limonene and *p*-cymene are respectively detected at 12.05 min and 12.41 min.

Figure 4 illustrates the semi-continuous monitoring of limonene and *p*-cymene expressed in µg per cubic meter and malodour olfactory perceptions in function of time.

It appears that the perception thresholds (around 10 µg / m^3 for each compound)[4,5] have been exceeded.

These results indicate a positive correlation between the concentration of tracers and the intensity of malodour.

It was observed that concentration of up to 29 µg/m^3 for limonene and 15 µg/m^3 for p-cymene and simultaneously olfactory responses intensities corresponded to a particular management activity on the site involving biogas leaking from the collecting network. The observations illustrated in Figure 5, showing the semi-continuous monitoring of *p*-cymene for a given period, strongly suggest that the nauseous emissions are mainly due to the leaks of bio-gas from the col-

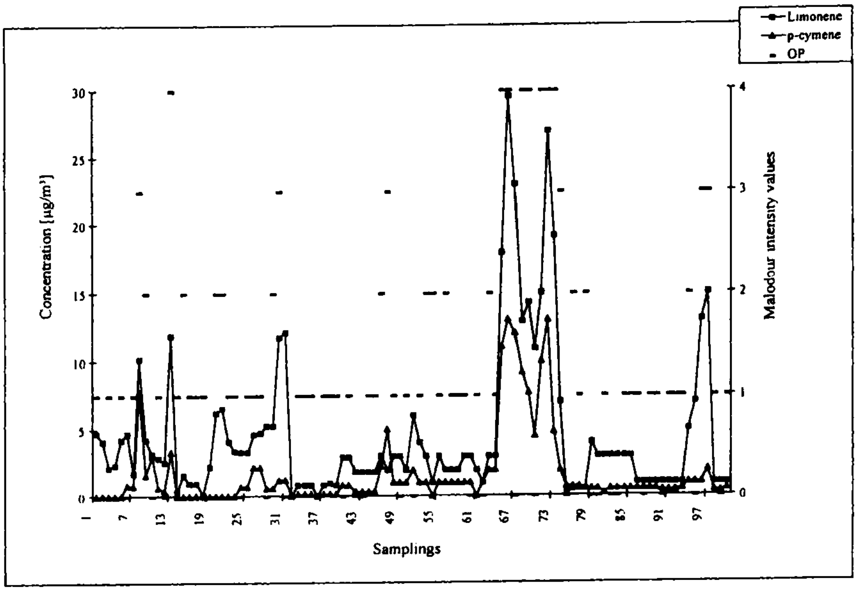

FIGURE 4 Semi-continuous monitoring of limonene and *para*-cymene expressed in µg/m^3 and malodour olfactory perceptions in function of time. The samplings consist in pumping every two hours (night- and daytime) 100 ml of ambient air. Olfactory perceptions (OP) values vary from 0 to 4 meaning respectively "no data", "absence of odour", "weak odour", "moderately nauseous" and "foul"

lecting net and / or from the flares. This is confirmed by the coincidence of complaints reported by local residents and the observations of a *p*-cymene peak, which is a biogas tracer.

When the municipal waste discharging is at rest (without human activity as digging holes, moving waste, creating waste tumuli,...) and if the flares are continuously burning at convenient temperature, the levels of limonene and *p*-cymene concentrations never exceeded 6 µg/m^3.

CONCLUSIONS

The observations performed in the course of this study indicate a strong positive correlation between specific odorous tracers and the intensity of malodours perceived in the environment of the landfill. More specifically, leaks of bio-gas seem to be the main responsible for nauseous emissions.

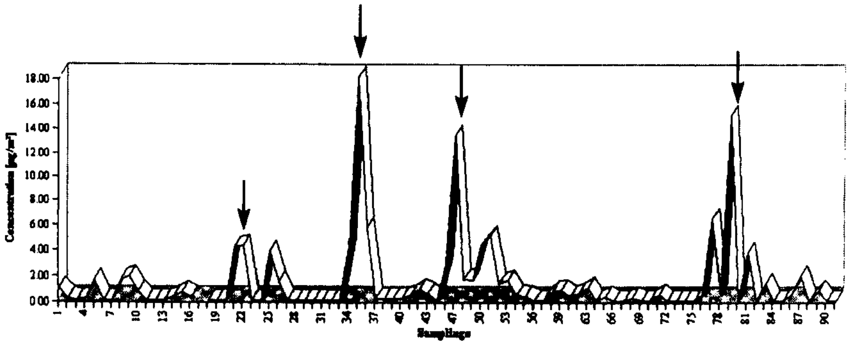

FIGURE 5 Semi-continuous monitoring of *p*-cymene expressed in µg/m^3 in function of time. The samplings consist in pumping every two hours (night- and daytime) 100 ml of ambient air. The arrows indicate the time of the sampling corresponding to a complaint lodged by the local residents living around the dump

The described procedure applied to municipal waste discharging appears to be an efficient technique to detect malfunctions in the bio-gas collecting facilities, causing olfactive nuisances and discomfort for the local residents.

Effectively, foul gas emissions released by the bio-gas can successfully be detected at the 1 µg/m^3 level by the gas analyser. It is a powerful tool for the landfill managers for the detection of leaks in the collecting system.

It is obvious that odours are linked to the presence of VOC, but it must be stressed that it is not realistic to extrapolate the contribution of each compounds to the perceived odour only thanks to a quantitative physico-chemical analysis. Indeed, we do not know the complex interaction and interference (inhibiting or exacerbating effects) between the compounds before reaching the olfactory receptor cells of the best sensor : the nose. However, it is perfectly possible to characterise and monitor one or more odorous tracer(s) in order to measure the impact of the gaseous emissions.

The analytical system can be used for the monitoring of many classes of compounds, including polar compounds because no water elimination system is used. In this way, the analytical procedure described in this paper (possibly with minor system adaptations) could be applied at different environmental issues related to atmospheric pollution. The monitor is automatic and can record data over monthes without considerable maintenance. It is important to note that with minor changes, the analytical set-up can be used whenever olfactive nuisances or VOC pollution have to be monitored. The environmental and health applications of such a system are numerous in various fields (e.g., the chemical, pharmaceutical and agro-food industry, indoor and outdoor air quality control pollution,...).

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