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Atmospheric emissions and attenuation of non-methane organic compounds in cover soils at a French landfill

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Abstract

In addition to methane (CH₄) and carbon dioxide (CO₂), landfill gas may contain more than 200 non-methane organic compounds (NMOCs) including C₂+-alkanes, aromatics, and halogenated hydrocarbons. Although the trace components make up less than 1% v/v of typical landfill gas, they may exert a disproportionate environmental burden. The objective of this work was to study the dynamics of CH₄ and NMOCs in the landfill cover soils overlying two types of gas collection systems: a conventional gas collection system with vertical wells and an innovative horizontal gas collection layer consisting of permeable gravel with a geomembrane above it. The 47 NMOCs quantified in the landfill gas samples included primarily alkanes (C₂–C₁₀), alkenes (C₂–C₄), halogenated hydrocarbons (including (hydro)chlorofluorocarbons ((H)CFCs)), and aromatic hydrocarbons (BTEXs). In general, both CH₄ and NMOC fluxes were all very small with positive and negative fluxes. The highest percentages of positive fluxes in this study (considering all quantified species) were observed at the hotspots, located mainly along cell perimeters of the conventional cell. The capacity of the cover soil for NMOC oxidation was investigated in microcosms incubated with CH₄ and oxygen (O₂). The cover soil showed a relatively high capacity for CH₄ oxidation and simultaneous co-oxidation of the halogenated aliphatic compounds, especially at the conventional cell. Fully substituted carbons (TeCM, PCE, CFC-11, CFC-12, CFC-113, HFC-134a, and HCFC-141b) were not degraded in the presence of CH₄ and O₂. Benzene and toluene were also degraded with relative high rates. This study demonstrates that landfill soil covers show a significant potential for CH₄ oxidation and co-oxidation of NMOCs.

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1. Introduction

Landfill gas is produced under anaerobic conditions by microbial degradation of the organic fraction in waste disposed of in landfill facilities. The main components in landfill gas are CH₄ (55–60% v/v) and CO₂ (40–45% v/v). In addition to CH₄ and CO₂, landfill gas may contain more than 200 non-methane organic compounds including C₂+-alkanes, aromatics, and halogenated hydrocarbons (Rettenberger and Stegmann, 1996; Allen et al., 1997;

Eklund et al., 1998; Barlaz et al., 2004). These trace gas constituents originate from household hazardous waste materials deposited in the landfill or from biological/chemical decomposition processes within the landfill. Hydrocarbon trace components are typically termed non-methane organic compounds (NMOCs) or non-methane hydrocarbons (NMHCs) and are usually quantified as individual species. In this paper, we will refer to speciated NMOCs. Due to pressure and concentration gradients, landfill gas is emitted to the atmosphere. Although the trace components make up less than 1% v/v of typical landfill gas, they may exert a disproportionate environmental burden. Emissions of carcinogens such as benzene and vinyl chloride

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may pose a potential threat to workers and local inhabitants (Christensen and Kjeldsen, 1995), whereas chlorofluorocarbons (CFCs) or hydrochlorofluorocarbons (HCFCs) contribute to the depletion of the ozone layer and climate change (Molina and Rowland, 1974; Wallington et al., 1994).

In landfill covers CH_4 and O_2 counter-gradients may appear due to emission of CH_4 from the waste and diffusion of O_2 from ambient air. Previous literature has shown that cover soils may develop a high capacity for CH_4 oxidation by indigenous aerobic methanotrophic microorganisms reducing the amount of CH_4 emitted to the atmosphere (Czepiel et al., 1996a,b; Liptay et al., 1998; Bogner et al., 1995,1997b,c; Christophersen et al., 2001). While attenuation of CH_4 in landfill covers has been intensively studied to evaluate the contribution of landfills to global warming, there is little research concerning the potential for attenuation of NMOCs. Only recently, it has been demonstrated that a number of NMOCs including halogenated hydrocarbons and aromatics can be degraded in landfill covers soils possessing methanotropic activity (Kjeldsen et al., 1997; Scheutz et al., 2003, 2004; Scheutz and Kjeldsen, 2005). Scheutz and Kjeldsen (2003, 2005) also found that halogenated organic compounds were dechlorinated in the anoxic part of laboratory column studies simulating landfill cover conditions whereas the generated degradation products were removed in the oxic part of the columns leading the authors to conclude that both aerobic and anaerobic degradation processes in landfill covers might have a significant attenuation effect on emissions from landfill settings. To date, there have been few studies which document either oxidation rates or atmospheric emissions of speciated NMOCs in landfill settings. The objective of this study was to investigate attenuation mechanisms and rates, as well as net emission rates, for selected NMOC species at Grand'Landes Landfill in western France near Nantes. A secondary objective of this study was also to contrast CH_4 and NMOC dynamics in the cover soils overlying two types of landfill gas collection systems. This study quantified emissions of NMOC species and their degradation rates in landfill cover soils using similar field and laboratory methods as the preliminary study conducted at Lapouyade Landfill near Bordeaux, France (Scheutz et al., 2003).

2. Materials and methods

2.1. Site description of Grand'Landes Landfill

Grand'Landes Landfill is located in western France near Nantes. This 26 ha landfill has been accepting municipal solid waste between 1989 and 2001 at a rate of app. 185,000 metric tons yr^{-1} . The current study focused on two cells, 25A and 25B, each containing app. 54,000 metric tons of waste. Cell 25A had five conventional vertical gas collection wells and a cover design consisting of a leveling layer, compacted clay (70 cm), and a topsoil vegetative layer (30 cm) (Fig. 1A). The total thickness of the compacted clay/topsoil sequence was app. 1 m. Cell 25B had an innovative gas collection system consisting of two horizontal perforated pipes within a gas collection layer consisting of 30 cm of gravel (Fig. 1B). The two pipes were placed perpendicular to each other with a common collection point at one corner of the cell. The gravel gas collection layer was underlain by a geo-grid (geo-composite) and was overlain, in turn, by a geo-textile protective layer, a 1.5 mm thick HDPE-membrane, a second geo-textile layer, 70 cm compacted clay, and 30 cm topsoil. The covers on both cells were installed in 1998 and appeared vegetated with different herbs and grasses. The CH_4 recovered rate at the two cells are app. 1100 kg $\text{CH}_4 \text{ d}^{-1}$ for cell 25A and 799 kg $\text{CH}_4 \text{ d}^{-1}$ for cell 25B (Spokas et al., 2006). The control area selected for this field campaign was a grassy field not underlain by waste, which lay near the site entrance and was adjacent to recently filled areas. The field campaign including source gas sampling, flux and gas profiles measurements, and soil sampling were conducted from September 10th to 15th, 2002. During the field campaign temperatures between 13 and 27 °C were recorded.

2.2. Source gas sampling

Concentrated landfill gas samples were taken from individual gas collection headers from cells 25A and 25B. These represented the average source gas composition at this landfill. Table 3 shows chemical names, synonyms and formula for speciated NMOCs analyzed for in this study.

Fig. 1. Schematic for Cell 25A cover materials and a vertical well (A) and for Cell 25B cover materials with a horizontal gas collection system (B).

2.3. Flux chamber measurements

Emission rates of CH₄, CO₂, and speciated NMOCs were determined using static flux chambers. Two iron collars functioned as bases for two static chambers (A and B); the bases were placed adjacent to each other at a depth of 4–5 cm in the cover soil. Chambers consisted of stainless steel hemispheres, each with a single stainless steel (SS) Swagelok sampling port at the top for either (1) direct sampling using syringes or (2) direct connection to an evacuated 2 L electropolished canister. During monitoring periods of 120 min, the troughs were filled with distilled water and secured with hand clamps. Chamber volume was 31,830 cm³ over an enclosed surface area of 1217 cm². The volume/area ratio (cm³ cm⁻²) was 26. The exact volume of each chamber deployment was determined separately from field measurements.

The large sampling canister size and relatively small chamber volume precluded taking a series of timed samples from each chamber; nevertheless, the large canister size was needed to achieve a 20 pptv lower limit of detection for most species, which was necessary to quantify small positive and negative fluxes for many species. The first sample was taken at time zero in chamber A; after 120 min an additional sample was taken in both chambers A and B. A sampling time of 120 min was sufficient to measure concentration differences in the chamber and short enough to avoid significant concentration build up. The sampling approach and analytical techniques were tested in a previously reported study conducted at Lapouyade landfill (Scheutz et al., 2003). For the current study, three canister samples/test were taken: an initial and final sample from one chamber, plus a final from the adjacent chamber. This allowed a maximum check on the observed flux from the adjacent chambers. The fluxes reported herein rely on the initial value from chamber A and the final value from chamber B (adjacent). Fluxes were calculated from the product of the change in concentration over time (dc/dt) and the (chamber volume/chamber area) ratio (Rolston, 1986). Negative fluxes indicated an uptake of gases from the atmosphere by soil microorganisms, as the flux chamber concentration decreased over time.

The emission rates of CH₄ and CO₂ were measured by taking a time series of gas samples from both chambers in a shorter test. Five gas samples of 25–50 mL were withdrawn using gas-tight syringes over 20–70 min and stored in pre-evacuated serum bottles. In general, the CH₄ concentration vs. time curves showed good linear fits ($r^2 > 0.9$) without any change in slope for the final sampling times. Furthermore, when a sampling interval of 200 min was tested at a location with relatively high CH₄ emissions (7.89 g m⁻² d⁻¹), the final data indicated only a minor flattening of the slope with $r^2 > 0.98$. Due to the lower concentrations of trace gases compared to CH₄ concentrations, the gas build-up effect was expected to be even less for the NMOCs assuming only diffusional fluxes.

In order to compare the performance of the two different gas collection systems, emission measurements were conducted at two different areas of the landfill. For CH₄ emissions, a transect of six fluxes each was completed for both cells 25A and 25B. The 25A fluxes included both proximal (near vertical well) and distal (between vertical well) locations. In addition, six “hot spots” were also selected; these were located by French colleagues using dynamic chambers during the same field campaign. NMOC emissions were measured at five locations (F5, F7–F11) at the conventional cell 25A. At the innovative cell NMOC emissions were only measured at one location (F3) as minimal emissions were expected from this area due to placement of a HDPE-membrane on top of the cell. NMOC emissions were also measured on a grassy field adjacent to the landfill entrance and recently filled areas in order to determine the background emission (BG). All locations for chamber measurements were flagged during the field campaign and surveyed thereafter by site personnel using a GPS system.

2.4. Soil gas profiles

Soil gas profiles were determined by installing gas probes at different depths in the soil cover. The soil gas probes consisted of stainless steel tubes (10 mm ID), which were closed in at the bottom and provided with slits over the lower 3 cm. The steel probes were hammered into the ground at different depths. At each sampling site, separate soil gas probes were inserted to various depths with about 30 cm lateral separations from each other. Probes were purged, and gas samples of the main components (CH₄, CO₂, O₂, and nitrogen (N₂)) were taken at 10, 20, 30, 40, 60, 80, and 100 cm depths. Samples of 25–50 mL for major gases were withdrawn with a syringe and stored in pre-evacuated glass serum bottles. For speciated NMOCs, gas samples were taken at specified depths in 2L canisters. Samples for major gases were always taken before NMOC sampling. Four soil profiles (F7–F9, and F11) were collected from the soil cover on top of the conventional cell 25A and two single profiles (F3 and F6) were collected in the innovative cell 25B. The soil gas probes were inserted close to the flux chambers. At each location the gas profiles were measured directly after conducting the flux measurement.

2.5. NMOC gas analysis

All canister gas samples were analyzed by the Blake-Rowland Laboratory at the University of California – Irvine. Table 3 shows chemical names, synonyms and formula for speciated NMOCs analyzed for in this study. This laboratory has two separate high-resolution analysis systems capable of identifying and quantifying over 100 NMHCs and halocarbons from whole gas samples using multi column/detector gas chromatography (GC) and combined GC–MS (mass spectrometry) approaches.

The analytical apparatus utilized three GCs and five detectors. Each whole air sample was cryogenically trapped with liquid N₂, warmed, and injected into a helium flow stream. This stream was then split into five, with each stream feeding a separate GC column. One DB-1, one PLOT Al₂O₃/KCl, one Restek-1701, and two DB-5MS columns were used. One of the DB-5MS columns was plumbed into an electron capture detector (ECD) and separated C₁–C₂ halocarbons and the other DB-5MS was plumbed into a mass-spectrometer. The Restek-1701 column was used for alkyl nitrate separation and was connected to an ECD. The DB-1 FID combination separated C₃–C₈ NMHCs. The PLOT column, also plumbed to a FID, was used for separating the C₂–C₅ NMHCs, some of which were not resolved adequately by the DB-1.

The preparation of standards for the halocarbons has been discussed previously (Colman et al., 2001). The technique employed a pressure balancing method using three different sections of a glass vacuum line. Pure gas was introduced into the first section of the line and was ultimately diluted to a mixing ratio that most closely matches the concentration of the gas in the atmosphere. The range for halocarbon standards was 0.5–600 pptv. Concentration accuracies ranged between 1% and 20%.

Calibration of the other NMOC compounds has been achieved by employing Scott calibration gases available in the 1–100 ppmv mixing ratio range (Scott, Plumsteadville, PA, USA). The measurement precisions for the halocarbons, hydrocarbons, and alkyl nitrates were in the 1–10% range.

2.6. Major gases and stable carbon isotopes

Major gases and stable carbon isotopes ($\delta^{13}\text{C}$) were analyzed at Florida State University, Department of Oceanography. For CH₄ and CO₂ concentrations below 1%, gas concentrations were determined on a Shimadzu 14A GC with a flame ionization detector and a methanizer, a 1 mL sampling loop, and a 2 m 0.32 cm diameter stainless steel column packed with Carbosphere. N₂ and O₂ + Ar were determined on a Shimadzu 8A GC with a thermal conductivity detector. Scott Specialty gases were used as standards (Scott, Plumsteadville, PA, USA).

Stable isotopic ratios were determined using a Finnigan Mat Delta S-Gas Chromatograph Combustion Isotope Ratio Mass Spectrometer (GCC-IRMS) following methods adapted from Merritt et al. (1995). For air samples, a cryogenic focusing device was used on the front end of the GC. The cryofocusing process was conducted in two steps. In the first step the CH₄ was trapped from 10 mL of air on a packed 0.32 cm diameter 10 cm long column of Porapak Q in an ethanol-liquid N₂ slush. After 3 min, the slush was removed, the Porapak Q column was warmed, and the CH₄ was focused onto the head of the analytical column that was held in liquid N₂. The analytical column was Poraplot Q. After an additional 3 min the analytical column was

warmed and the CH₄ passed through the Poraplot Q column into the combustion column. On the 960 °C combustion column, the CH₄ was converted to CO₂ and then entered the mass spectrometer. The standard deviation of replicate analyses was generally about 0.15‰.

Stable isotopic ratios for the anoxic vented gases were determined using direct injection on the GCC-IRMS. Samples were diluted to 1% CH₄ by addition with N₂. Samples were then analyzed by injecting 0.1–0.5 mL of sample into the GCC-IRMS inlet system (Merritt et al., 1995).

2.7. Soil sampling and analysis

Soil profiles were collected at two locations (25A,F9 and 25B,F6) using a hand auger. Generally, soil was sampled at 5–10 cm intervals down to a depth of 55 cm below the surface, described at the time of sampling, and stored at 4 °C in darkness in closed plastic bags to avoid dehydration prior to the analysis and laboratory experiments. The soil was sieved through an 8 mm mesh to increase homogeneity. The following soil analyses were carried out: soil moisture content, total organic carbon, total organic nitrogen, pH, Cu, NH₄⁺, NO₃[−], Cl[−] and SO₄^{2−}. All soil concentrations are expressed on a mass dry soil basis. Soil analyses are described in Scheutz et al. (2003).

2.8. Soil microcosms

CH₄ oxidation and degradation of trace components were examined in soil microcosms at the Institute of Environment & Resources, Technical University of Denmark. The compounds studied included chlorinated methanes, ethanes, and ethenes; five halocarbons; and two aromatic hydrocarbons (see Table 6). A fixed amount of soil (20 g incl. soil water) was added to a 117 mL batch container equipped with a butyl rubber stopper, which enabled gas to be sampled or injected by a syringe. To obtain CH₄ oxidation conditions, air was withdrawn from each container using a syringe and replaced with CH₄ and O₂, which gave an initial mixture of 15% CH₄, 30% O₂, and 55% N₂ (v/v). The degradation of the trace components was determined by periodic sampling of the gas phase and analysis by GC (Scheutz et al., 2004). From the measured gas concentrations, the total mass (μg) of compound was determined by phase distribution calculations using Henry's Law and the octanol/water distribution coefficient (Scheutz et al., 2004). In order to check if disappearance of a compound could be due to non-microbial processes (abiotic degradation, sorption and volatilization), sterilized controls were prepared by autoclaving and/or adding sodium azide (25 mg kg^{−1}), depending on the test. All aerobic batch experiments were conducted in duplicate at room temperature (22 °C).

Batch experiments were conducted with soil sampled at both the conventional waste cell (25A) and the innovative waste cell (25B). In general, the batch experiments were carried out with soil from the 5–10 cm depth at cell

25A(F9) and from the 30–40 cm depth at cell 25B(F6). However, to examine oxidation rates as a function of depth, tests were also conducted with soils from various depths.

3. Results and discussion

3.1. Soil cover design and properties

Table 1 shows the soil parameters of the cover soils at both the conventional waste cell (25A) and the innovative cell (25B). The soil cover in place at the conventional cell (25A) of Grand'Landes Landfill consisted of app. 30 cm of top soil on top of 70 cm of clay. Generally, these soils were silty with variable clay and sand content. The soil moisture content varied between 13% and 19% w/w, with maximum moisture content at 25 cm depth. The total organic carbon content varied between 1.5% and 3.2% w/w with the maximum content at 25 cm depth. The soil at 25 cm depth also had the highest content of total organic nitrogen. The pH of the soil water varied between 5.5 and 7.6 with minimum values observed just below the surface. Very high ammonium concentrations (up to 255 mg N kg⁻¹) were measured in the deeper part of the soil cover. In the 25A area, colours were generally darker with depth, consistent with reduced aeration at the top of refuse. Soil sampled at 50 cm below the surface had a strong smell of landfill gas.

The soil top cover in place at the innovative cell (25B) of Grand'Landes Landfill consisted of app. 30 cm of top soil on top of 70 cm of clay, underlain by an HDPE-membrane. The soil moisture content versus depth was relatively constant with a slight maximum of 11.5% w/w at 15–20 cm depth. The organic carbon content varied between 1.7% and 3.2% w/w with the highest concentration at 30–40 cm depth. Similar trends were observed for total nitrogen with a maximum concentration of 2440 mg kg⁻¹. The pH of the soil water varied between 5.8 and 7.6 with minimum values

in the top section of the cover. The ammonium content was low throughout the profile. The measured anions NO₃⁻, Cl⁻, SO₄²⁻ generally showed increasing concentrations with depth.

The temperature of the cover soils at both cells measured 10 cm below the surface varied between 17 and 25 °C. The highest temperatures were recorded in the afternoon, whereas the lowest temperatures were recorded in the early morning.

3.2. Landfill gas composition

The composite landfill gas in both the 25A and 25B collection headers had significant air intrusion: 32% v/v N₂ and 7% v/v O₂ in 25A and 42% v/v N₂ and 5% v/v O₂ in 25B (Table 2). Since gas sampled from individual wells or deeper soil profiles had CH₄ concentrations as high as 50–75% v/v, this air intrusion was associated with the collection system. The 25A N₂/O₂ ratio was close to the expected atmospheric ratio (4/1) while the 25B-ratio was app. twice the atmospheric ratio, indicating depletion in O₂ (c.f. Table 2). The δ¹³C of CH₄ sampled at the flair headers were −59.00‰ and −56.91‰ for cell 25A and cell 25B, respectively (Table 2). Gas sampled from deeper

Table 2

Source gas concentrations (% v/v) and isotopic compositions (‰) at Grand'Landes Landfill from collection headers near flare and from deep soil probes at 25A

	25A	25B	Deep gas profile at 25A
Methane	37	29	73
Carbon dioxide	25	25	24
Oxygen	7	5	1
Nitrogen	32	42	4
Sum	102	101	101
δ ¹³ C of CH ₄	−59.00 ± 0.60‰	−56.91 ± 0.08‰	−63.11 ± 0.17‰
δ ¹³ C of CO ₂	+12.1 ± 0.3‰	+3.3 ± 0.9‰	+16.48 ± 20.6‰

Table 1

Soil parameters for the cover soils at the conventional waste cell (25A) and the innovative cell (25B)

Depth cm.b.s.	H ₂ O (% w/w)	TOC (% w/w)	TON (mg kg ⁻¹)	pH	Cu (mg kg ⁻¹)	NH ₄ ⁺ (mg N kg ⁻¹)	NO ₃ ⁻ (mg N kg ⁻¹)	Cl ⁻ (mg kg ⁻¹)	SO ₄ ²⁻ (mg S kg ⁻¹)
<i>Soil cover parameters at the conventional waste cell (25A)</i>									
0–5	13.95	1.80	1190	5.5	1.9	<1.0	1.7	13.4	3.8
5–10	13.66	1.86	1250	5.8	2.5	4.9	3.5	12.4	8.2
15–20	15.17	1.83	1200	6.4	2.7	5.2	43.0	0.6	0.4
20–30	18.83	3.15	2200	7.6	1.2	3.8	69.0	26.7	0.0
30–40	13.23	1.89	862	7.0	3.3	4.6	49.0	49.7	96.3
40–50	13.08	1.51	477	6.0	1.1	126.5	28.0	121.7	43.0
50–55	13.73	1.67	748	7.1	1.1	255.0	18.0	235.3	111.6
<i>Soil cover parameters at the innovative waste cell (25B)</i>									
0–10	10.76	1.84	1150	5.8	1.2	3.8	8.7	16.9	3.9
10–15	9.48	1.66	1130	5.9	1.4	2.5	5.0	34.9	14.0
15–20	11.52	1.71	893	5.8	1.4	<1.0	5.7	46.0	15.1
20–30	10.80	1.74	1150	6.4	2.7	<1.0	6.9	123.3	30.7
30–40	10.23	3.22	2440	7.6	1.0	5.5	35.0	152.4	62.0

TOC: Total organic carbon. TON: Total organic nitrogen.

soil probes within landfill cell 25A had a CH₄ δ¹³C value of −63.1‰, while biogas recovered from probes installed at site 25B was −62.1‰. As CH₄ is oxidized, its concentration in the biogas decreases, its ¹³C value becomes more positive, CO₂ concentration increases and the ¹³C value of CO₂ becomes more negative as ¹³C depleted carbon is added to the biogas CO₂ pool. The change in isotopic composition of both CH₄ and CO₂ between samples taken in deeper gas probes within the cells and the gas collection headers indicated CH₄ oxidation in the collection system.

All 47 NMOCs included in the analysis program were detected and quantified in the landfill gas samples. Table 3 lists trace gas concentrations from collection headers near the flare. A wide variety of NMOCs were quantified; these included alkanes (C₂–C₁₀), alkenes (C₂–C₄), alkyl nitrates, halogenated hydrocarbons (including (H)CFCs), and aromatic compounds (BTEXs). As the composition of the major gases indicated air intrusion into the gas collection system, the true NMOC concentrations can be expected to be higher – by app. a factor of two based on the N₂ content. However, in spite of dilution, the NMOC concen-

Table 3
Trace gas concentrations at Grand'Landes Landfill from collection headers near flare

Header from area:		25A		25B	
Trace gas constituent	Formula	10 ³ pptv	µg L ⁻¹	10 ³ pptv	µg L ⁻¹
Ethane	C ₂ H ₆	1768	2.3	1584	2.1
Propane	C ₃ H ₈	1860	3.5	1444	2.7
<i>n</i> -Butane	C ₄ H ₁₀	2519	6.2	1599	3.9
<i>n</i> -Pentane	C ₅ H ₁₂	564	1.7	1067	3.3
<i>n</i> -Hexane	C ₆ H ₁₄	206	0.8	182	0.7
<i>n</i> -Heptane	C ₇ H ₁₆	1240	5.3	882	3.8
<i>n</i> -Octane	C ₈ H ₁₈	725	3.5	250	1.2
<i>n</i> -Nonane	C ₉ H ₂₀	1950	10.6	436	2.8
<i>n</i> -Decane	C ₁₀ H ₂₂	2697	16.3	455	2.7
<i>i</i> -Butane	C ₄ H ₁₀	2036	5.0	1201	3.0
<i>i</i> -Pentane	C ₅ H ₁₂	1287	3.9	2676	8.2
2-Methylpentane	C ₆ H ₁₄	410	1.5	482	1.8
3-Methylpentane	C ₆ H ₁₄	221	0.8	270	1.0
Ethene	C ₂ H ₄	2316	2.8	1467	1.7
Propene	C ₃ H ₆	4353	7.8	2805	5.0
1-Butene	C ₄ H ₈	103	0.3	99	0.2
<i>i</i> -Butene	C ₄ H ₈	121	0.3	178	0.4
<i>t</i> -2-Butene	C ₄ H ₈	108	0.3	103	0.2
<i>c</i> -2-Butene	C ₄ H ₈	107	0.3	86	0.2
Ethyne	C ₂ H ₂	60	0.2	38	0.1
Isoprene	C ₅ H ₈	41	0.1	33	0.1
Methyl nitrate	CH ₃ ONO ₂	0.003	9.8·10 ⁻⁶	0.01	3.9·10 ⁻⁵
Ethyl nitrate	C ₂ H ₅ ONO ₂	0.003	1.2·10 ⁻⁵	0.01	4.3·10 ⁻⁵
Iso-propyl nitrate	i-C ₃ H ₇ ONO ₂	0.1	6.2·10 ⁻⁴	0.2	1.1·10 ⁻³
<i>n</i> -Propyl nitrate	n-C ₃ H ₇ ONO ₂	0.001	4.0·10 ⁻⁶	0.004	1.8·10 ⁻⁵
2-Butyl nitrate	C ₄ H ₉ ONO ₂	0.01	4.8·10 ⁻⁵	0.003	1.3·10 ⁻⁵
Tetrachloromethane (TeCM)	CCl ₄	0.1	7.2·10 ⁻⁴	2	1.0·10 ⁻²
Trichloromethane (TCM)	CHCl ₃	0.9	4.6·10 ⁻³	4	2.0·10 ⁻²
Dichloromethane (DCM)	CH ₂ Cl ₂	50	0.2	113	0.4
Chloromethane (MCM)	CH ₃ Cl	270	0.6	325	0.7
1,1,1-Trichloroethane (1,1,1-TCA)	C ₂ H ₃ Cl ₃	1	1.0·10 ⁻³	8	4.0·10 ⁻²
Perchloroethene (PCE)	C ₂ Cl ₄	234	1.7	89	0.6
Trichloroethene (TCE)	C ₂ HCl ₃	33	0.2	19	0.1
1,2-dichloroethene (1,2-DCE)	1,2-DCE	12	0.1	2	1.0·10 ⁻²
Dichlorodifluoromethane (CFC-12)	CCl ₂ F ₂	114	0.7	841	4.9
Trichlorofluoromethane (CFC-11)	CCl ₃ F	596	3.1	317	1.6
1,1,2-Trichlorotrifluoroethane (CFC-113)	C ₂ Cl ₃ F ₃	2	1.0·10 ⁻²	2	1.0·10 ⁻²
Chlorobromodifluoromethane (H-1211)	CBrClF ₂	0.2	1.7·10 ⁻³	0.1	8.1·10 ⁻⁴
Chlorodifluoromethane (HCFC-22)	CHClF ₂	503	1.8	340	1.3
1,1-dichloro-1-fluoroethane (HCFC-141b)	CCl ₂ FCH ₃	4354	21.6	11,625	57.7
1,1,1,2-tetrafluoroethane (HFC-134a)	CH ₂ FCF ₃	626	2.7	369	1.6
Benzene	C ₆ H ₆	224	0.7	91	0.3
Toluene	C ₇ H ₈	5270	20.6	1760	6.9
Ethylbenzene	C ₈ H ₁₀	7508	33.5	2996	13.5
<i>m,p,o</i> -Xylene	C ₈ H ₁₀	11,740	53.9	3439	15.5

trations were generally low with relatively little variation between 25A and 25B. However, *n*-octane, *n*-nonane, and *n*-decane were elevated in 25A compared to 25B; the highest among these in 25A was *n*-decane at about $16 \mu\text{g L}^{-1}$. It is not unusual to see the higher alkanes elevated in landfill gas samples; *n*-nonane and *n*-decane had also been elevated in the Lapouyade source gas (up to $36 \mu\text{g L}^{-1}$) (Scheutz et al., 2003). Halogenated compounds at Grand'Landes exhibited low concentrations, generally less than $1.5 \mu\text{g L}^{-1}$, much lower than at Lapouyade where PCE and dichloromethane (DCM) were present at concentrations of 47 and $10 \mu\text{g L}^{-1}$, respectively. The only trace components with concentrations greater than $10 \mu\text{g L}^{-1}$ at Grand'Landes were the aromatics (especially in 25A), *n*-nonane and *n*-decane in 25A as discussed above, and HCFC-141b at concentrations of $22 \mu\text{g L}^{-1}$ in 25A gas and $58 \mu\text{g L}^{-1}$ in 25B gas. Of the aromatics, ethylbenzene had the highest concentrations, $34 \mu\text{g L}^{-1}$ in 25A gas and $14 \mu\text{g L}^{-1}$ in 25B gas. Consistent with results from Lapouyade, benzene exhibited the lowest concentrations among the aromatics for both 25A and 25B. This is also consistent with other investigations of landfill gas reported in the literature where the aromatics are often elevated compared to other trace components, but the concentration of benzene is significantly lower than concentrations of the other aromatics. For example, Rettenberger and Stegmann (1996) reported on five sites where toluene, ethylbenzene, and xylenes ranged between 0.2 and $615 \mu\text{g L}^{-1}$ while benzene ranged between 0.03 and $15 \mu\text{g L}^{-1}$. Since benzene is a listed carcinogen, the low observed concentrations from several sites should reduce the level of concern regarding the health and environmental aspects of landfill gas.

In general, the NMOC concentrations in landfill gas at Grand'Landes were lower than at Lapouyade Landfill and lower than most values reported in the literature (Brosseau and Heitz, 1994; Rettenberger and Stegmann, 1996; Allen et al., 1997; Eklund et al., 1998). Data from UK landfills (e.g., the Allen et al., 1997 study) would be expected to exhibit higher concentrations of trace components due to historic co-disposal practices in the UK. Moreover, it should be kept in mind that cells 25A and 25B were filled during the two years preceding the field campaign; thus it is likely that peak concentrations of many volatile species have not yet been achieved.

3.3. Landfill gas emission

Surface emissions of CH_4 and NMOC species are given in Table 4. Generally, with the exception of a few hot spots, located mainly along cell perimeters, all of the CH_4 fluxes were very low indicating that cover designs for both cells were functioning extremely well to mitigate CH_4 emissions and even functioning to take up atmospheric CH_4 from the atmosphere.

At cell 25A, negative CH_4 flux values were observed at 6 of 12 chamber deployments at rates ranging from -0.3 to $-2.5 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$. At five deployments, positive rates

were observed (indicating emission of CH_4 from the landfill to the atmosphere) at rates ranging from 0.0001 to $29 \text{ g m}^{-2} \text{ d}^{-1}$. One site showed no net flux. The five zones of CH_4 emissions in area 25A were all hotspots located during a screening of surface fluxes using dynamic flux chambers and were sampled to support the concurrent NMOC studies. In situ determination of CH_4 oxidation is based upon measuring the difference in $\delta^{13}\text{C}$ between anoxic zone CH_4 and CH_4 emitted from the landfill cover soil, which has been subjected to oxidation. Combined with measurement of the preference of the bacteria for $^{12}\text{CH}_4$ relative to $^{13}\text{CH}_4$, a quantitative estimate of the fraction of CH_4 oxidized as it passes through the landfill cover soil can be determined (Chanton et al., 1999; Liptay et al., 1998). The average fractional CH_4 oxidation varied between 0% and 54% oxidation using -59‰ as anoxic zone CH_4 . If -63.1‰ was used for anoxic zone CH_4 , an oxidation of between 7% and 68% was obtained in the 5 chambers at cell 25A where a flux of CH_4 was measured (Chanton et al., 2003), showing that even at hotspots some oxidation was occurring.

At cell 25B, with the HDPE-membrane, CH_4 uptake from the atmosphere (negative emissions) was observed at all 6 chamber deployments with rates from -0.2 to $-2.2 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$. Thus the surface soils above the HDPE-membrane were a sink for atmospheric CH_4 . Negative fluxes or atmospheric uptake indicated net oxidation of atmospheric CH_4 with no landfill CH_4 emission at the location of the static chamber. In such cases the methanotrophs in the cover soil not only oxidize CH_4 that may originate from the waste but also CH_4 that is transported into the soil from atmosphere sources above the landfill. Negative CH_4 fluxes have been previously reported in other field studies (Bogner et al., 1995, 1997b, 1999). Measured CH_4 emissions from the background area (grassy field) were app. $4.8 \text{ g m}^{-2} \text{ d}^{-1}$; it is not entirely clear why these were somewhat elevated. It is possible that CH_4 was being generated in the subsurface in anaerobic zones resulting from previous precipitation events, since the control area was placed in a hollow close to the site entrance area. Lateral gas migration from the landfill is not considered very likely due to placement of synthetic liners containing the disposed waste.

All of the 47 NMOCs samples quantified in the composite landfill gas samples from the collection headers were also identified in the static chambers. In general, NMOC fluxes across cell 25A were all very small with positive and negative fluxes in the order of 10^{-8} – $10^{-5} \text{ g m}^{-2} \text{ d}^{-1}$ (Table 4). The highest percentages of positive fluxes in this study (considering all quantified species) were observed at the two hotspots. In particular, the higher alkanes and alkenes exhibited higher fluxes on the order of 10^{-6} – $10^{-4} \text{ g m}^{-2} \text{ d}^{-1}$ at these two locations. Negative fluxes were generally observed for all of the aromatics on both of the landfill cells and the control area with rates as high as $10^{-4} \text{ g m}^{-2} \text{ d}^{-1}$. The only exceptions, where positive fluxes were observed for the aromatics, were the two hotspots

Table 4
Surface emissions at Grand'Landes Landfill ($\text{g m}^{-2} \text{d}^{-1}$)

Cell station	Cell 25A F5	F7 ^a	F8 ^a	F9 ^a hotspot	F10 hotspot	F11 ^a hotspot	Cell 25B F3 ^a	Field BG
Methane	0.0000	-0.0011	0.0001	29.03	24.03	1.45	-0.002	4.78
Ethane	$3.45 \cdot 10^{-6}$	$4.64 \cdot 10^{-6}$	$4.11 \cdot 10^{-6}$	$3.22 \cdot 10^{-5}$	$5.45 \cdot 10^{-5}$	$4.26 \cdot 10^{-6}$	$3.73 \cdot 10^{-6}$	$8.99 \cdot 10^{-6}$
Propane	$2.33 \cdot 10^{-6}$	$2.08 \cdot 10^{-6}$	$3.92 \cdot 10^{-6}$	$5.98 \cdot 10^{-5}$	$7.00 \cdot 10^{-5}$	$1.25 \cdot 10^{-6}$	$-3.03 \cdot 10^{-6}$	$5.24 \cdot 10^{-6}$
<i>n</i> -Butane	$1.73 \cdot 10^{-6}$	$7.77 \cdot 10^{-7}$	$2.53 \cdot 10^{-6}$	$4.73 \cdot 10^{-5}$	$4.91 \cdot 10^{-5}$	$3.85 \cdot 10^{-7}$	$-2.39 \cdot 10^{-6}$	$2.15 \cdot 10^{-6}$
<i>n</i> -Pentane	$6.23 \cdot 10^{-6}$	$6.19 \cdot 10^{-6}$	$5.77 \cdot 10^{-6}$	$3.47 \cdot 10^{-5}$	$7.37 \cdot 10^{-5}$	$1.15 \cdot 10^{-6}$	$7.77 \cdot 10^{-6}$	$1.28 \cdot 10^{-5}$
<i>n</i> -Hexane	$1.18 \cdot 10^{-6}$	$4.80 \cdot 10^{-7}$	0	$2.03 \cdot 10^{-6}$	$2.23 \cdot 10^{-6}$	$3.53 \cdot 10^{-6}$	$1.76 \cdot 10^{-7}$	$1.19 \cdot 10^{-6}$
<i>n</i> -Heptane	$-1.41 \cdot 10^{-7}$	$-1.30 \cdot 10^{-7}$	$-5.87 \cdot 10^{-6}$	$3.44 \cdot 10^{-7}$	$1.44 \cdot 10^{-6}$	$1.91 \cdot 10^{-7}$	$-3.92 \cdot 10^{-7}$	$1.21 \cdot 10^{-6}$
<i>n</i> -Octane	$-1.16 \cdot 10^{-7}$	$-9.55 \cdot 10^{-8}$	$-3.30 \cdot 10^{-6}$	$1.01 \cdot 10^{-5}$	$3.53 \cdot 10^{-6}$	$3.63 \cdot 10^{-7}$	$-4.76 \cdot 10^{-7}$	$-1.01 \cdot 10^{-6}$
<i>n</i> -Nonane	$9.31 \cdot 10^{-6}$	$1.19 \cdot 10^{-8}$	$-2.68 \cdot 10^{-5}$	$2.71 \cdot 10^{-7}$	$-3.60 \cdot 10^{-7}$	$1.77 \cdot 10^{-6}$	$-1.20 \cdot 10^{-5}$	$-8.69 \cdot 10^{-6}$
<i>n</i> -Decane	$-2.56 \cdot 10^{-7}$	$-1.27 \cdot 10^{-5}$	$-3.76 \cdot 10^{-4}$	$1.63 \cdot 10^{-5}$	$1.11 \cdot 10^{-5}$	$-3.00 \cdot 10^{-5}$	$-4.71 \cdot 10^{-6}$	$-1.94 \cdot 10^{-5}$
<i>i</i> -Butane	$1.88 \cdot 10^{-6}$	$1.84 \cdot 10^{-7}$	$-1.10 \cdot 10^{-6}$	$7.29 \cdot 10^{-5}$	$7.39 \cdot 10^{-5}$	$9.49 \cdot 10^{-8}$	$3.11 \cdot 10^{-7}$	$6.69 \cdot 10^{-7}$
<i>i</i> -Pentane	$5.14 \cdot 10^{-7}$	$4.22 \cdot 10^{-7}$	$-1.71 \cdot 10^{-6}$	$2.11 \cdot 10^{-4}$	$1.03 \cdot 10^{-4}$	$5.89 \cdot 10^{-7}$	$-1.23 \cdot 10^{-7}$	$1.15 \cdot 10^{-6}$
2-Methylpentane	$2.70 \cdot 10^{-7}$	$2.24 \cdot 10^{-7}$	$1.59 \cdot 10^{-8}$	$5.00 \cdot 10^{-6}$	$4.33 \cdot 10^{-6}$	$-2.89 \cdot 10^{-7}$	$2.20 \cdot 10^{-8}$	$4.22 \cdot 10^{-7}$
3-Methylpentane	$2.70 \cdot 10^{-8}$	$1.60 \cdot 10^{-8}$	$-3.50 \cdot 10^{-7}$	$7.72 \cdot 10^{-6}$	$3.02 \cdot 10^{-6}$	$-2.74 \cdot 10^{-7}$	$-2.13 \cdot 10^{-7}$	$1.33 \cdot 10^{-7}$
Ethene	$7.35 \cdot 10^{-5}$	$3.50 \cdot 10^{-5}$	$2.84 \cdot 10^{-5}$	$6.87 \cdot 10^{-6}$	$1.94 \cdot 10^{-5}$	$2.14 \cdot 10^{-6}$	$4.80 \cdot 10^{-5}$	$1.99 \cdot 10^{-4}$
Propene	$3.56 \cdot 10^{-6}$	$1.62 \cdot 10^{-6}$	$3.05 \cdot 10^{-6}$	$9.25 \cdot 10^{-6}$	$2.68 \cdot 10^{-5}$	$2.25 \cdot 10^{-6}$	$2.24 \cdot 10^{-5}$	$4.22 \cdot 10^{-6}$
1-Butene	$-6.46 \cdot 10^{-7}$	$2.50 \cdot 10^{-7}$	$-5.74 \cdot 10^{-7}$	$4.91 \cdot 10^{-6}$	$2.59 \cdot 10^{-6}$	$8.55 \cdot 10^{-7}$	$-5.53 \cdot 10^{-7}$	$6.70 \cdot 10^{-7}$
<i>i</i> -Butene	$-3.25 \cdot 10^{-7}$	$1.05 \cdot 10^{-6}$	$5.64 \cdot 10^{-7}$	$7.40 \cdot 10^{-6}$	$3.42 \cdot 10^{-6}$	$2.29 \cdot 10^{-6}$	$1.42 \cdot 10^{-6}$	$3.28 \cdot 10^{-6}$
<i>t</i> -2Butene	$2.20 \cdot 10^{-8}$	$4.69 \cdot 10^{-8}$	$-1.82 \cdot 10^{-6}$	$1.56 \cdot 10^{-6}$	$2.18 \cdot 10^{-6}$	$9.11 \cdot 10^{-7}$	$-7.68 \cdot 10^{-7}$	$2.27 \cdot 10^{-7}$
<i>c</i> -2-Butene	$-8.79 \cdot 10^{-8}$	$5.21 \cdot 10^{-8}$	$-2.27 \cdot 10^{-6}$	$1.03 \cdot 10^{-6}$	$1.91 \cdot 10^{-6}$	$7.38 \cdot 10^{-7}$	$-5.49 \cdot 10^{-7}$	$1.69 \cdot 10^{-7}$
Ethyne	$5.12 \cdot 10^{-7}$	$-3.99 \cdot 10^{-7}$	$-3.14 \cdot 10^{-8}$	$-1.78 \cdot 10^{-6}$	$9.79 \cdot 10^{-7}$	$-3.70 \cdot 10^{-6}$	$6.84 \cdot 10^{-7}$	$6.56 \cdot 10^{-7}$
Isoprene	$5.39 \cdot 10^{-7}$	$4.30 \cdot 10^{-7}$	$6.16 \cdot 10^{-6}$	$-2.22 \cdot 10^{-7}$	0	0	$4.11 \cdot 10^{-7}$	$-4.27 \cdot 10^{-7}$
Methyl nitrate	$-1.09 \cdot 10^{-8}$	$-7.16 \cdot 10^{-9}$	$-3.48 \cdot 10^{-8}$	$-1.15 \cdot 10^{-8}$	$3.29 \cdot 10^{-7}$	$-1.40 \cdot 10^{-8}$	$-2.49 \cdot 10^{-8}$	$5.30 \cdot 10^{-9}$
Ethyl nitrate	$-1.36 \cdot 10^{-8}$	$5.92 \cdot 10^{-9}$	$-2.18 \cdot 10^{-8}$	$7.22 \cdot 10^{-9}$	$2.03 \cdot 10^{-7}$	$-1.57 \cdot 10^{-8}$	$2.01 \cdot 10^{-8}$	$1.48 \cdot 10^{-7}$
Iso-propyl nitrate	$8.56 \cdot 10^{-8}$	$5.76 \cdot 10^{-8}$	$-5.33 \cdot 10^{-8}$	$1.22 \cdot 10^{-7}$	$2.59 \cdot 10^{-7}$	$-2.10 \cdot 10^{-8}$	$2.29 \cdot 10^{-7}$	$3.45 \cdot 10^{-7}$
<i>n</i> -propyl nitrate	$-1.15 \cdot 10^{-8}$	$4.88 \cdot 10^{-9}$	$3.88 \cdot 10^{-9}$	$-1.85 \cdot 10^{-9}$	$-6.94 \cdot 10^{-9}$	$-9.54 \cdot 10^{-10}$	$-1.70 \cdot 10^{-8}$	$1.84 \cdot 10^{-7}$
2-Butyl nitrate	$-6.63 \cdot 10^{-8}$	$7.08 \cdot 10^{-8}$	$4.40 \cdot 10^{-9}$	$-4.62 \cdot 10^{-8}$	$-9.54 \cdot 10^{-8}$	$1.08 \cdot 10^{-9}$	$-1.11 \cdot 10^{-8}$	$6.59 \cdot 10^{-7}$
CFC-12	$-2.27 \cdot 10^{-7}$	$5.39 \cdot 10^{-7}$	$6.02 \cdot 10^{-7}$	$-2.13 \cdot 10^{-8}$	$-1.11 \cdot 10^{-6}$	$1.21 \cdot 10^{-7}$	$-2.16 \cdot 10^{-7}$	$-1.56 \cdot 10^{-7}$
CFC-11	$3.73 \cdot 10^{-5}$	$1.33 \cdot 10^{-6}$	$7.86 \cdot 10^{-7}$	$4.36 \cdot 10^{-7}$	$7.94 \cdot 10^{-8}$	$4.11 \cdot 10^{-7}$	$6.54 \cdot 10^{-7}$	$2.66 \cdot 10^{-6}$
CFC-113	$-4.74 \cdot 10^{-8}$	$1.01 \cdot 10^{-7}$	$-7.81 \cdot 10^{-8}$	$4.26 \cdot 10^{-8}$	$-9.98 \cdot 10^{-9}$	$2.19 \cdot 10^{-8}$	$-2.06 \cdot 10^{-8}$	$4.16 \cdot 10^{-8}$
H-1211	$-3.89 \cdot 10^{-9}$	$4.61 \cdot 10^{-9}$	$-3.05 \cdot 10^{-9}$	$4.37 \cdot 10^{-9}$	$-1.09 \cdot 10^{-8}$	$-6.00 \cdot 10^{-9}$	$-8.44 \cdot 10^{-9}$	$2.84 \cdot 10^{-9}$
HCFC-22	$-6.10 \cdot 10^{-8}$	$1.85 \cdot 10^{-7}$	$-2.39 \cdot 10^{-8}$	$4.64 \cdot 10^{-6}$	$9.07 \cdot 10^{-6}$	$-3.14 \cdot 10^{-8}$	$-1.54 \cdot 10^{-7}$	$-5.20 \cdot 10^{-8}$
HCFC-141b	$4.75 \cdot 10^{-6}$	$6.66 \cdot 10^{-5}$	$7.98 \cdot 10^{-6}$	$1.01 \cdot 10^{-5}$	$1.02 \cdot 10^{-5}$	$3.63 \cdot 10^{-6}$	$4.38 \cdot 10^{-6}$	$3.23 \cdot 10^{-5}$
HFC-134a	$2.40 \cdot 10^{-8}$	$2.75 \cdot 10^{-7}$	$4.14 \cdot 10^{-7}$	$5.41 \cdot 10^{-6}$	$5.49 \cdot 10^{-6}$	$-2.50 \cdot 10^{-7}$	$-2.59 \cdot 10^{-6}$	$1.75 \cdot 10^{-8}$
Tetrachloromethane	$-4.82 \cdot 10^{-8}$	$2.29 \cdot 10^{-7}$	$-1.28 \cdot 10^{-7}$	$-2.71 \cdot 10^{-8}$	$-2.54 \cdot 10^{-8}$	$9.77 \cdot 10^{-8}$	$-2.62 \cdot 10^{-8}$	$-1.32 \cdot 10^{-8}$
Trichloromethane	$3.14 \cdot 10^{-5}$	$4.46 \cdot 10^{-5}$	$1.80 \cdot 10^{-5}$	$-1.29 \cdot 10^{-6}$	$1.84 \cdot 10^{-5}$	$2.58 \cdot 10^{-5}$	$-5.03 \cdot 10^{-6}$	$-6.15 \cdot 10^{-6}$
Dichloromethane	$-3.13 \cdot 10^{-7}$	$-2.60 \cdot 10^{-7}$	$-6.74 \cdot 10^{-7}$	$-8.53 \cdot 10^{-7}$	$-7.01 \cdot 10^{-8}$	$-9.33 \cdot 10^{-7}$	$-2.75 \cdot 10^{-7}$	$-6.42 \cdot 10^{-7}$
Chloromethane	$3.37 \cdot 10^{-7}$	$-4.41 \cdot 10^{-7}$	$-2.36 \cdot 10^{-6}$	$2.64 \cdot 10^{-7}$	$-1.69 \cdot 10^{-7}$	$-6.00 \cdot 10^{-6}$	$-8.08 \cdot 10^{-7}$	$-2.71 \cdot 10^{-7}$
1,1,1-Trichloroethane	$-3.79 \cdot 10^{-8}$	$6.74 \cdot 10^{-8}$	$-6.69 \cdot 10^{-8}$	$1.07 \cdot 10^{-8}$	$-3.00 \cdot 10^{-8}$	$5.49 \cdot 10^{-8}$	$-4.11 \cdot 10^{-8}$	$3.12 \cdot 10^{-8}$
Perchloroethene	$-6.24 \cdot 10^{-7}$	$1.85 \cdot 10^{-7}$	$1.38 \cdot 10^{-7}$	$4.38 \cdot 10^{-7}$	$1.31 \cdot 10^{-6}$	$3.61 \cdot 10^{-7}$	$-1.41 \cdot 10^{-7}$	$3.85 \cdot 10^{-7}$
Trichloroethene	$1.85 \cdot 10^{-8}$	$-4.76 \cdot 10^{-8}$	$-4.30 \cdot 10^{-7}$	$4.02 \cdot 10^{-7}$	$4.92 \cdot 10^{-7}$	$-1.50 \cdot 10^{-7}$	$-2.24 \cdot 10^{-9}$	$1.32 \cdot 10^{-7}$
1,2-dichloroethene	$-3.80 \cdot 10^{-9}$	$2.70 \cdot 10^{-9}$	$6.26 \cdot 10^{-9}$	$-3.08 \cdot 10^{-8}$	$-2.24 \cdot 10^{-8}$	$-1.32 \cdot 10^{-8}$	$-4.95 \cdot 10^{-9}$	$-5.00 \cdot 10^{-9}$
Benzene	$-8.87 \cdot 10^{-7}$	$-2.03 \cdot 10^{-7}$	$-1.53 \cdot 10^{-6}$	$8.26 \cdot 10^{-8}$	$1.67 \cdot 10^{-6}$	$-3.16 \cdot 10^{-6}$	$-1.43 \cdot 10^{-6}$	$-7.38 \cdot 10^{-8}$
Toluene	$-1.43 \cdot 10^{-6}$	$-3.24 \cdot 10^{-6}$	$-4.68 \cdot 10^{-5}$	$-3.24 \cdot 10^{-6}$	$9.94 \cdot 10^{-6}$	$-2.41 \cdot 10^{-6}$	$-5.71 \cdot 10^{-6}$	$4.05 \cdot 10^{-6}$
Ethylbenzene	$-3.08 \cdot 10^{-7}$	$-3.33 \cdot 10^{-6}$	$-8.56 \cdot 10^{-5}$	$5.92 \cdot 10^{-6}$	$2.28 \cdot 10^{-7}$	$-2.76 \cdot 10^{-6}$	$-2.16 \cdot 10^{-6}$	$-3.31 \cdot 10^{-6}$
m,p,o-Xylene	$-9.48 \cdot 10^{-7}$	$-3.27 \cdot 10^{-5}$	$-4.04 \cdot 10^{-4}$	$3.38 \cdot 10^{-5}$	$5.12 \cdot 10^{-6}$	$-2.33 \cdot 10^{-5}$	$-6.76 \cdot 10^{-6}$	$-3.27 \cdot 10^{-5}$

^a Installation of soil gas probes.

with the highest CH_4 emissions of app. 29 and $24 \text{ g m}^{-2} \text{ d}^{-1}$ respectively. Fukui and Doskey (1998) also investigated the air-surface exchange of selected aromatic hydrocarbons (including benzene, toluene, and *o*-, *m*-, and *p*-xylene) and consistently measured an uptake of these compounds into the soil, which they concluded was due to sorption to soil material. From the Lapouyade results and a previous Illinois study where soil gas profiles indicated an inward gradient from the atmosphere to the soil (Bogner et al., 1997a), it is likely that the aromatics are generally being oxidized out of the atmosphere by surface soils.

Above the HDPE-membrane on cell 25B, most of the NMOC fluxes were also negative at rates ranging from 10^{-9} to $10^{-6} \text{ g m}^{-2} \text{ d}^{-1}$. The atmospheric concentrations of NMOCs above the soil surface were comparable with air concentrations measured in areas with moderate to high urbanization (c.f. Table 5). As NMOC concentrations in the ambient air above the two landfill cells (first sample in the flux chamber) showed no difference in concentration from air sampled at the background location, it is possible that the elevated NMOC concentrations were attributed to dispersal from the operational part of the landfill or, more

likely for the aromatics, to the vehicle exhaust from waste trucks.

The NMOC emissions in this study were comparable to NMOC fluxes quantified in the previous Lapouyade landfill study, where the NMOC fluxes from a final cover zone were all very small with positive and negative fluxes in the order of 10^{-7} – $10^{-5} \text{ g m}^{-2} \text{ d}^{-1}$. The NMOC fluxes measured in this study were generally lower than fluxes reported in a comparison study of the attenuation performance of a soil cover versus a biocover conducted at the Outer Loop Landfill in Louisville, KY, USA (Barlaz et al., 2004). In the Illinois (USA) landfill study by Bogner et al. (1997a), emissions of most NMOC species were generally 10^{-5} – $10^{-3} \text{ g m}^{-2} \text{ d}^{-1}$; these somewhat higher emissions are probably due to the thin interim soil cover over recently landfilled waste.

3.4. Soil gas concentration profiles

3.4.1. Conventional cell (25A)

Fig. 2 shows soil gas profiles for major gases and selected NMOCs at location F8 from cell 25A. Generally,

Table 5

Comparison of air concentrations (pptv) measured in this study with available mean air concentration data presented in the review by Pankow et al. (2003) and references herein

Compound	Grand'Landes Landfill		Degree of urbanization				
	Background (BG)	Ambient air above landfill	Very high	High	Moderate	Low	Total interval
CFC-12	602	566 ± 30	990	490–830	390–490	460	390–990
CFC-11	414	306 ± 69	800	220–260	70–210	210	70–800
CFC-113	83	81 ± 4	200	60–120	20–60	60	20–200
Trichloromethane	3538	606 ± 950		9–100	5.0–9.0	6	40–140
1,1,1-Trichloroethane	37	37 ± 3		60–520	20–70	70	20–520
Tetrachloromethane	104	102 ± 4		100–140	40–110	130	5–100
Dichloromethane	214	191 ± 74		90–720	30–40	50	30–720
Trichloroethene	10	40 ± 26		7–410	20–30	2	7–410
Perchloroethene	32	64 ± 17		40–330	20	10	10–260
Benzene	98	242 ± 140	17,500	430–1700	170–360	230	170–17,500
Toluene	669	1361 ± 1754	27,800	850–6400	230–560	290	230–27,800
Ethylbenzene	425	1370 ± 3002	8600	120–990	30–90	40	30–8600

Fig. 2. Soil gas profiles at station F8 at the conventional cell; 25A.

the soil gas profiles taken at cell 25A showed that the soil gas mainly consisted of air throughout the profile. The profiles showed only low concentrations of CH_4 ($<0.1\%$ v/v), with the highest concentrations appearing close to the surface and in the deeper part of the profile. Decreasing CH_4/CO_2 -ratios from 100 to 60 cm depth indicated CH_4 oxidation activity in this zone. At this depth, a small decline in O_2 and an increase in CO_2 were also observed. In some profiles a decrease in $\delta^{13}\text{C}-\text{CO}_2$ was observed between 100 and 60 cm depths, also indicating microbial activity. In general, the CH_4 concentrations and also often the CO_2 concentrations were too low to analyze the isotopic composition.

The profiles sampled at the hotspots, where high CH_4 emissions were measured ($24\text{--}29\text{ g m}^{-2}\text{ d}^{-1}$) showed high concentrations of CH_4 and CO_2 at 60 cm depth and below. Fig. 3 shows soil gas profiles for major gases and selected NMOCs sampled at a hotspot (F9, cell 25A). The decrease in the CH_4/CO_2 ratio when moving upward in the profiles indicates CH_4 oxidation throughout the profile. Between 80 and 40 cm depth, the isotopic analysis shows an increase in $\delta^{13}\text{C}-\text{CH}_4$ and a decrease in $\delta^{13}\text{C}-\text{CO}_2$ indicating CH_4 oxidation in this zone. The steeper decrease in $\delta^{13}\text{C}$ in CO_2 between 60 and 40 cm depth compared to the increase in $\delta^{13}\text{C}$ in CH_4 indicates activity of other soil respiring microorganism. Isotopic fractionations of CH_4 within the profiles using the method of Chanton (Chanton et al., 1999; Liptay et al., 1998) indicated that between 25% and 35% of the CH_4 was oxidized at the hotspots based on a $\delta^{13}\text{C}-\text{CH}_4$ value of -61‰ for the anoxic CH_4 .

Generally, large differences in soil gas profiles for the different NMOCs were observed within the same location. Often soil gas concentrations increased over several orders of magnitude from air values taken at the ground surface to soil gas at the top of the refuse. For some NMOCs very constant gas profiles were obtained while others showed increasing gas concentrations toward the surface (Figs. 2 and 3). However, some NMOCs showed similar behavior within chemical groups. In order to provide an overview

of the correlation between different components, plots showing individual concentrations versus each other in the same samples were conducted. The correlation plots include all measured NMOC concentrations (both emissions and soil gas concentrations). In general, the BTEXs and also the non-halogenated aliphatic hydrocarbons were very well correlated with each other, which probably is due to similar sources but also similar behavior in the soil covers concerning biodegradation, sorption, etc. (Fig. 4A and B). This was not the case for other groups like the chlorinated methanes and ethenes, indicating that compounds within these groups had individual behavior in the soil (Fig. 4C).

Generally, the gas concentration profiles of the aromatics, the alkenes, and the alkanes showed a similar trend both between compounds and between the gas profiles as a minimum around 40 cm depth was observed with increasing concentrations towards the surface. In contrast, the gas profiles for the chlorinated ethenes and methanes were very different. However, similarities between profiles sampled at different locations were observed, e.g., the concentration profiles for DCM and TCE were similar with a minimum in concentrations between 40 and 60 cm depth, which was in accordance with the zone where the gas composition of main components indicates microbial activity. At all locations (excluding hotspots) very constant concentration profiles for TCA, TeCM, CFC-113, and CFC-12 were observed.

At the two hotspots the NMOC-concentrations were generally higher in the deeper part of the profiles compared to the profiles sampled at locations with low emissions, which was expected as the gas composition of the main components resembles the composition of landfill gas. Generally, the NMOC concentration profiles were similar for the BTEXs and the hydrocarbons $\text{C}_2\text{--C}_{10}$, and showed a decrease in concentrations towards the surface. Also for most of the halogenated compounds, a decrease in concentrations of orders of magnitude towards the surface was observed with the exception of a few compounds like TCA, TeCM and CFC-113 showing more constant gas profiles.

Fig. 3. Soil gas profiles at station F9 (hot spot) at the conventional cell; 25A.

Fig. 4. Correlation plot based on all measured concentrations for ethenes (A), aromatics (B), and halogenated organic carbons (C).

3.4.2. Innovative cell (25B)

Fig. 5 shows soil gas profiles for major gases and selected NMOCs at location F3 from cell 25B. The composition of the main components in the soil cover at the innovative cell showed O_2 and N_2 in relatively high concentrations compared to atmospheric concentrations throughout the profiles. CH_4 was also detected – the concentrations were however very low (<7 ppm) and comparable to the elevated CH_4 concentration measured in the ambient air above the landfill (2.24–174 ppm). The CH_4 profiles showed no clear trend in depth distribution; however, at location F6 the highest CH_4 concentrations were measured near the surface (Fig. 9A). Elevated concentrations of CO_2 were observed in all profiles, with concentrations increasing with depth. This, together with a decline in the O_2 concentration indicated soil respiration. The CH_4 concentrations were in general too low to allow measuring the isotopic composition ($\delta^{13}C-CH_4$).

Generally, the NMOC-concentrations in the soil profile at cell 25B were lower compared to the NMOC-concentrations measured at the two hotspots at cell 25A but they

were comparable to the NMOCs concentrations measured at the conventional cell where an uptake of CH_4 was observed (Fig. 5). The soil gas profiles of the NMOCs showed differences in the profiles for the different NMOCs. Often an increase in gas concentration was observed towards the surface, indicating an uptake from the atmosphere. An exception was TeCM, PCE, CFC-11, CFC-12, CFC-113, and HCFC-141b (Fig. 5).

3.5. Methane oxidation in soil microcosms

3.5.1. Conventional cell (25A)

In all soil microcosms, CH_4 and O_2 concentrations declined over time while CO_2 increased, suggesting that CH_4 oxidation was taking place (c.f. Fig. 6A). Lag phases were never observed, which indicated that the bacteria were well adapted to oxidizing CH_4 . The oxidation was microbially mediated, as seen from a comparison with the sterilized control batch (Fig. 6B). Maximal oxidation rates were calculated by applying zero order kinetics to the data, excluding the last data points (CH_4 conc. < 3% v/v) where the

Fig. 5. Soil gas profiles at station F3 at the innovative cell; 25B.

Fig. 6. Headspace concentration of methane, oxygen and carbon dioxide as function of time, showing methane oxidation in a batch experiment containing 20 g soil sampled at 5–10 cm below the soil surface at cell 25A (F9). (A) Active batch experiment. (B) Control experiment.

reaction rate changes to a first-order due to substrate limitation. Generally more than 90% of all the data points were included in the calculation of the oxidation rate, giving linear regression coefficients higher than 0.8. Table 6 lists maximal oxidation rates and regression coefficients. The soil showed a relatively high capacity for CH_4 oxidation resulting in oxidation rates of up to $674 \mu\text{g CH}_4 \text{ g soil}^{-1} \text{ d}^{-1}$. The CH_4 oxidation rates were significantly higher than the rates obtained with soil from Lapouyade landfill ($18\text{--}35 \mu\text{g CH}_4 \text{ g soil}^{-1} \text{ d}^{-1}$) in the previous study (Scheutz et al., 2003). The obtained oxidation rates were also in the higher end of maximal CH_4 oxidation rates for landfill cover soils reported in the literature, which range between 0.06 and $3072 \mu\text{g CH}_4 \text{ g}^{-1} \text{ d}^{-1}$ (Christophersen et al., 2000).

3.5.2. Innovative cell (25B)

The soil sampled at the innovative cell (25B) also showed a capacity for CH_4 oxidation even though significantly lower oxidation rates were obtained (7 to $28 \mu\text{g CH}_4 \text{ g soil}^{-1} \text{ d}^{-1}$). The CH_4 oxidizers in the soil cover placed on the innovative cell were probably mainly fed by CH_4 from the ambient air as only little CH_4 was emitted from the waste due to the placement of a membrane. The soil cover placed on the innovative cell is probably quite representative for soils exposed to atmospheric CH_4 concentrations, which often exhibit kinetics with low activity. Maximal CH_4 oxidation rates for natural soils reported in the literature vary between 0.02 and $17 \mu\text{g CH}_4 \text{ g}^{-1} \text{ d}^{-1}$ when incubated with low initial CH_4 concentrations ($< 1\% \text{ v/v}$) (Christophersen et al., 2000). However, Bender and Conrad (1995) obtained maximum CH_4 oxidation rates of $1306 \mu\text{g CH}_4 \text{ g}^{-1} \text{ d}^{-1}$ for different natural soils when incubated with high initial CH_4 concentrations (up to $20\% \text{ v/v}$), which is comparable to results obtained in this study.

3.6. Degradation of trace components in soil microcosms

3.6.1. Conventional cell (25A)

Fig. 7 shows the relative headspace concentration of selected NMOCs versus time. In general, very good reproducibility was obtained and results from duplicate batches

were almost identical. Maximal oxidation rates were calculated by applying a zero-order kinetic to the data describing 90% of the mass transformation. Maximal oxidation rates, initial concentrations, and regression coefficients are listed in Table 6. All lower chlorinated compounds were

Table 6

Maximal methane oxidation and degradation rates ($\mu\text{g g soil}^{-1} \text{ d}^{-1}$) obtained from batch experiments containing methane and selected NMOCs. Soil water content was 20% w/w. Average rates calculated from duplicates

Compound studied	Initial gas conc. $\mu\text{g L}^{-1}$	Cell 25A				Cell 25B	
		Degradation rate		R^2	R^2	R ²	R ²
Methane		674				28	
<i>Methanes</i>							
DCM	70	11.2	>0.87			8.7	>0.88
TCM	400	0.3	>0.79				
TeCM	20	n.d.					
<i>Ethanes</i>							
1,1-DCA	1000	3.7	>0.87				
1,2-DCA	200	5.2	>0.77				
1,1,1-TCA		n.d.					
<i>Ethenes</i>							
VC	100	4.2	>0.91			3.3	>0.95
c-1,2-DCE	800	5.4	>0.96				
t-1,2-DCE	800	6.3	>0.75				
1,1-DCE	500	0.2	>0.80				
TCE	50	0.4	>0.96				>0.82
PCE	20	n.d.					
<i>Halocarbons</i>							
CFC-11	50	n.d.					
CFC-12	50	n.d.					
CFC-113	50	n.d.					
HCFC-141b	100	n.d.					
HFC-134a	200	n.d.					
HCFC-21	550	3.7	>0.93			0.2	
HCFC-22	450	2.2	>0.94			0.1	
<i>Aromatics</i>							
Benzene	300	3.0	>0.93			0.6	>0.83
Toluene	200	2.0	>0.92			0.1	>0.93

Regression coefficient (R^2) obtained from fitting the experimental data to a zero-order rate model.

n.d.: No degradation observed.

Fig. 7. Relative headspace concentration of chlorinated hydrocarbons as a function of time in batch experiments, containing 20 g soil pre-exposed to landfill gas sampled at 5–10 cm below the soil surface at cell 25A(F9). (A) Chlorinated methanes. (B) Chlorinated ethylenes. (C) Chlorinated ethanes. (D) Chlorofluorocarbons. (E) (Hydro)chlorofluorocarbons. (F) Aromatic hydrocarbons. Full chemical names are given in Table 3. Please note the different time scales.

degradable and the degradation rates were inversely related to the chlorine/carbon ratios. For example in batch experiments with chlorinated methanes, the highest rates were observed for DCM and the lowest rates obtained for TCM, while TeCM were not degraded. The degradation occurred in parallel with the oxidation of CH_4 . Maximal oxidation rates for the halogenated aliphatic compounds varied between 0.2 and $11.2 \mu\text{g g}^{-1} \text{d}^{-1}$. These rates are comparable with oxidation rates for a number of halogenated compounds reported for Lapouyade landfill (0.1 – $38.7 \mu\text{g g}^{-1} \text{d}^{-1}$) (Scheutz et al., 2003) and for Skellingsted landfill (0.72 and $41 \mu\text{g g}^{-1} \text{d}^{-1}$) (Scheutz et al., 2004). Fully substituted carbons (TeCM, PCE, CFC-11, CFC-12 and CFC-113) were not degraded in presence of CH_4 and O_2 . Also HFC-134a and HCFC-141b did not seem to be degradable within the duration of the experiment.

In general the sterilized control experiments showed no decrease in the NMOC concentration, indicating that microbial oxidation was the only explanation for the decrease in the active experiments.

3.6.2. Innovative cell (25B)

The potential of the soil cover placed at the innovative cell to stimulate degradation of trace components was investigated in soil experiments with HCFC-21, HCFC-22, DCM, VC, benzene, and toluene. The soil sampled at the innovative cell (25B) also showed a capacity for degradation of trace components, but as for CH_4 significantly lower oxidation rates were obtained. In general the highest rates, which were obtained with soil sampled at 35 cm depth, were a factor of 20 lower compared to the maximum rates obtained with soil from the conventional cell. Exceptions were VC and DCM, which were degraded with rates

comparable to the rates observed with soil from the conventional cell (c.f. Table 6).

3.7. Depth distribution of oxidation activity

3.7.1. Conventional cell (25A)

Fig. 8 shows the maximal oxidation rates obtained as a function of depth at the conventional waste cell 25A. The CH_4 oxidizers were active in oxidizing CH_4 and trace components down to a depth of 40 cm below the surface. Generally, the forms of the oxidation curves were similar for CH_4 and both HCFCs and aromatic hydrocarbons, showing a maximum around 5–10 cm depth. However, a somewhat broader optimum range was observed for VC and DCM: 5–30 cm below the surface. This depth distribution of CH_4 oxidation capacity and the depth interval with peak oxidation observed in 5–15 cm depth is consistent with results observed in other landfill soil covers (Czepiel et al., 1996a; Whalen et al., 1990; Scheutz et al., 2004). Reduced methanotrophic activity in the upper soil layers is thus often observed and has been suggested to result from microbial competition for mineral nutrients (Bender and Conrad, 1994), inhibition by ammonium released by organic matter (Adamsen and King, 1993), or less than optimal moisture conditions (Whalen and Reeburgh, 1992). Reduced activity below the maxima in landfill cover soils often appears to be due to O_2 limitation (Scheutz et al., 2003). The soil gas profiles at the hotspots indicated that below 60 cm the oxidation capacity was limited by available O_2 as the soil gas consisted of almost pure landfill gas (Fig. 8A). However, another factor inhibiting CH_4 oxidation at Grand'Landes could be the ammonium content, which increased from 4.6 mg N kg^{-1} close to the surface

Fig. 8. (A) Soil gas depth profiles at station 25A F9. (B–D) Maximal methane oxidation and degradation rates of trace components in batch experiments as a function of soil sampling depth.

to $126.5 \text{ mg N kg}^{-1}$ at 40 cm depth. Ammonium has been found to be inhibitory in soil concentrations above 14 mg N kg^{-1} (Scheutz and Kjeldsen, 2004; Boeckx and van Cleemput, 1996). It is therefore very likely that the methanotrophs in the deeper part of the soil cover was inhibited by ammonium.

3.7.2. Innovative cell (25B)

Fig. 9 shows the maximal oxidation rates obtained as a function of depth at the innovative waste cell 25B. The CH_4 oxidation capacity in the soil cover placed at the innovative cell was generally lower compared to the conventional cell.

Also, the depth distribution of the CH_4 oxidizers was different from the conventional cell. High oxidation capacity was observed just below the soil surface at 0–10 cm where after the oxidation rates decreased reaching a minimum around 15–20 cm depth and increased again to reach maximum oxidation capacity at 35 cm depth. In general, the same pattern was observed for the halogenated compounds whereas the increase in degradation rates of the aromatic hydrocarbons with depth was less evident. In natural soils where the methanotrophs are exposed to atmospheric CH_4 concentrations, reduced activity below the maxima is expected due to limited substrate CH_4 availability. Czepiel

Fig. 9. (A) Soil gas depth profiles at station 25B F6. (B–D): Maximal methane oxidation and degradation rates of trace components in batch experiments as a function of soil sampling depth.

et al. (1995) found maximum oxidation rates in soil cores sampled at a grassy field and a temperate forest area at 3–6 cm below the surface. Similar results were obtained by Adamsen and King (1993) who observed maximal oxidation rates at 3–9 cm in natural soils. The increasing oxidation activity following depth observed at cell 25B could indicate a source of CH_4 coming from beneath. Sources could be diffusion of CH_4 through the HDPE-membrane, or horizontal diffusion of CH_4 through the cover from the neighboring conventional cell. Calculations showed a diffusive flux of $0.13 \text{ g CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ of CH_4 through a HDPE-membrane with a thickness of 1.5 mm when using a diffusion coefficient of $1.18 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ (Kjeldsen, 1993). Based on the CH_4 oxidation rates obtained in batch experiments, a degradation rate integrated over the depth of the cover at the innovative cell can be calculated to $16.8 \text{ g CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ (c.f. Scheutz et al., 2004). The emission of CH_4 through the HDPE-membrane should thus be oxidized in the soil cover as the oxidation capacity exceeds the diffusive CH_4 flux under the circumstances that the gas transport can be considered intergranular.

3.8. Comparison of flux measurements, soil gas profiles, and biodegradability

In general, the cover soil at cell 25A showed a high capacity for CH_4 oxidation, which corresponded well with the gas profiles, the isotopic data, and the low or negative emissions suggesting significant CH_4 oxidation. At the conventional cell soil gas profiles showed, with the exception of the hotspots, presence of O_2 down to a depth of 80 cm providing living conditions for the methanotrophs. This relatively large oxidation zone was most likely due to the efficient gas extraction system favoring O_2 transport into the soil. The soil gas profiles showed very low CH_4 concentrations in the cover soil with CH_4 concentrations similar to the elevated CH_4 concentrations measured in the ambient air. The efficient gas recovery system surely reduced the surface emissions. Soil gas profiles showing decreasing CH_4/CO_2 -ratios and decreasing $\delta^{13}\text{C}-\text{CO}_2$ profiles from 100 to 60 cm depth, however, indicated CH_4 oxidation. The importance of CH_4 oxidation was supported by the relatively high CH_4 oxidation capacity found in the batch experiments, explaining the flux measurements showing only very low emissions or even up-take. The soil gas profiles for the BTEXs, DCM, and TCE showed an increase in concentrations towards the surface indicating net diffusion of these compounds into the soil. Negative flux measurements of these compounds also indicated uptake from the atmosphere. With few exceptions a correlation between inward gradients and negative flux measurements was observed.

At all hotspots, where CH_4 emissions were measured, gas profiles also indicated a shallower oxidative zone with anaerobic conditions 60 cm below the surface. Isotopic fractionation analysis of CH_4 showed 25–35% oxidation in the cover. Even though the composition of the main

components suggested CH_4 oxidation throughout the soil profile, the shift in the gas concentration profiles and in the isotopic composition indicated a more profound CH_4 oxidation activity between 40 and 60-cm depth (c.f. Fig. 3). At the hotspots, a general decline in NMOC concentrations was measured from 80 cm to the surface, which mainly was attributed to dilution with atmospheric air, which become evident when the concentrations are corrected for dilution by dividing with $1-\text{N}_{2,\text{measured}}/\text{N}_{2,\text{air}}$. Despite the dilution, many of the NMOC concentrations profiles showed a decline between 40 and 60 cm depth, which corresponded to the CH_4 oxidative zone indicated by gas profiles for the main components and the isotopic fractionation. The results of the incubation experiments showed that the CH_4 oxidizers and the bacteria degrading the trace components were distributed in the upper 30 cm of the soil profile (Fig. 8B–D), which was higher than implied by the gas profiles. It is possible that the gas profiles measured that particular day were not representative for most other days during the year. Under other climatic conditions, it cannot be excluded that the oxidation zone is moved upwards. Furthermore, one must be careful when concluding on degradation, since the gas profiles do not only reflect degradation, but also different and opposing transport processes, and other chemical and physical processes such as, e.g., sorption and dilution. Also, at this location, there was no correlation between gas profiles for different NMOCs and the degradability observed in the laboratory experiments. Several of the halogenated trace gases like PCE, TCE, CFC-11, and CFC-12 are known to undergo reductive dechlorination under anaerobic conditions (Scheutz and Kjeldsen, 2003, 2005) and the gas profiles do then not only reflect oxidation in the aerobic zone but also anaerobic degradation in the deeper part of the soil profile. It is also likely that the system was not in steady state, as the hotspots represented leaks with relative high landfill gas fluxes where gas was emitted through cracks or fissures. Under such circumstances the degradation of the NMOCs was expected to be limited due to a short retention time. Flux measurements showed emissions of almost all the NMOCs at this location. Also, it should be kept in mind that the hotspots were placed on a leaky area located at the edge of the waste cell where the soil cover may not have been homogenous and it is therefore possible that the soil gas profile was not representative for the spot where the soil was sampled even though it was only 50 cm away.

At the innovative cell only negative CH_4 emissions were measured, demonstrating that the methanotrophs in the soil cover oxidized both the CH_4 diffusing through the HDPE-membrane and the CH_4 from ambient air, which seems reasonable due to the much higher oxidation potential compared to the diffusive CH_4 emission through the membrane. It was not possible to correlate the NMOC gas concentration profiles with the depth distribution of the oxidation activity, which partly was due to the fact that soil samples were only collected down to a 35 cm depth

whereas gas samples were collected down to a 70 cm depth. However, gas profiles showed higher concentrations in the ambient air for many of the trace gases compared to the measured concentration in the deeper part of the profile, indicating an uptake from the air, which was consistent with the flux measurement showing an uptake of most NMOC-components. However, there was no correlation between uptake rates and biodegradability of various NMOCs based on the incubation experiments. The results are, however, interesting since they indicate that soils exposed to atmospheric concentrations of different volatile organic compounds may develop a capacity for degradation and act as a negative feedback mechanism on increasing atmospheric NMOC concentrations.

Several transport processes like diffusion, advection, dilution, dissolution, sorption, and degradation govern the migration of landfill gas in soil. An additional complicating factor is that the processes take place in a bi-directional flow system, which is influenced by both meteorological and geo-physical factors. Despite the fact that soil gas profiles only represent an instant picture and reflect a variety of processes, comparative profiles for several gases can provide information about vertical zonation of various processes. However, in this study it was not possible to determine degradation zones based on the NMOC gas profiles alone, but the similar behavior between certain compounds was evident, as was also observed in the Lapouyade landfill study (Scheutz et al., 2003).

4. Conclusions and perspectives

This study demonstrates that landfill soil covers show a significant potential for CH₄ oxidation and biodegradation of NMOCs. Under certain conditions, landfills may even function as sinks of not only CH₄ but also selected NMOCs, like aromatic hydrocarbons and lower chlorinated compounds. At Grand'Landes Landfill, both landfill gas collection systems worked extremely well to reduce CH₄ and NMOC emissions from the atmosphere. The innovative gas collection and emission control system resulted in negligible CH₄ emissions and would continue to do so as long as the membrane remains intact. The only observed leakages occurred at the edges of the cell. Uptake of atmospheric CH₄ was occurring in the vegetated soil above the membrane. However, the cost of a HDPE-membrane is still significant and as this study demonstrates that a conventional gas extraction system in combination with a soil cover provides a very efficient gas emission control system at disposal sites. The challenge with such a system is to obtain a homogenous soil cover also on slopes and along intersections between waste cells. An alternative to a clay cover, which tends to desiccate creating cracks and fissures with significant gas emission during dry periods, could be a compost cover. Compost covers have shown high CH₄ oxidation capacities, and problems with desiccation are expected to be less pronounced due to the higher water holding capacity of compost materials.

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