

FIELD MEASUREMENT OF SPECIATED HAP [HAZARDOUS AIR POLLUTANT] EMISSIONS FROM LANDFILL COVER SOILS

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The emissions of methane (CH₄) and more than 30 HAPs (hazardous air pollutants) were quantified at two French landfills: Lapouyade (southwestern France near Bordeaux) and Grand'Landes (western France near Nantes). Using a static chamber technique, we investigated three areas at Lapouyade: the Phase I final cover area; the Phase II temporary cover area; and a forest control area. At Grand'Landes, emissions from three areas were measured: cell 25B with final cover including a geomembrane; cell 25A with conventional soil cover; and a field control area. Methane emissions from the final cover areas had high spatial variability including both positive and negative fluxes; however, all of the methane fluxes from cell 25B (with geomembrane and active gas recovery) were negative, indicating uptake of atmospheric CH₄ by soils overlying the geomembrane. Speciated HAP fluxes from the final cover areas at the two sites were small with both positive and negative fluxes ranging between 10⁻⁸ and 10⁻⁵ g·m⁻²·d⁻¹. The highest HAP emissions were from the temporary cover area at Lapouyade with fluxes that were mainly positive ranging between 10⁻⁵ and 10⁻⁴ g·m⁻²·d⁻¹. Generally, emitted compounds consisted of species recalcitrant to aerobic degradation (especially higher chlorinated compounds such as PCE and CFCs), while uptake from the atmosphere (negative emission) was observed for aerobically degradable species such as the aromatics. This study demonstrated that 1) the aerobic oxidation of CH₄ and selected HAPs in cover soils effectively lowers emissions to the atmosphere; and 2) as a result of bidirectional gaseous transport through landfill cover soils combined with their degradation capacity for HAPs and CH₄, cover soils function both as sources and sinks for atmospheric CH₄ and HAPs. It is thus important to understand both the direction and magnitude of species-specific fluxes in order to adequately quantify net emissions of CH₄ and HAPs.

BACKGROUND

The biodegradable fractions of landfilled municipal solid waste (MSW) decompose anaerobically and generate landfill gas, which consists primarily of methane (CH₄) and carbon dioxide (CO₂). In many developed countries, including the U.S., landfill CH₄ is strongly implicated in global change scenarios as the major anthropogenic source of atmospheric CH₄. Recently, Bogner and Matthews (2003) published annual estimates for global emissions.

Landfill gas also contains trace quantities (ppmv to pptv) of many other hydrocarbons, including C₂ and higher alkanes, aromatics, halogenated hydrocarbons, and organic sulfur compounds. Many of the trace components are listed HAPs (hazardous air pollutants) according to the U.S. EPA Clean Air Act (CAA) and Urban Air Toxics strategy. Section 112(d) of the CAA mandates the regulation of HAPs, and Section 112(b) [with updates] lists specific HAPs. This list now includes more than 180 species and classes of compounds (see <http://www.epa.gov/ttn/atw/hapindex.html>). For municipal solid waste landfills, the recent NESHAP/MACT (National Emissions Standards for Hazardous Air Pollutants)/ (Maximum Achievable Control Technology) regulations specifically mention vinyl chloride and certain aromatics (ethylbenzene, toluene, benzene) as the major HAPs emitted from landfills (*Fed. Register 88, 11, Thursday, Jan 16,*

2003/Rules and Regulations/p. 2227). Practically speaking, the NESHAP/MACT standards re-establish the previous NSPS/EG (New Source Performance Standards/Emission Guidelines) for landfill gas as the regulatory guidance—these regulations stipulate that sites estimated to emit more than 50 Mg/year of total non-methane organic compounds shall be required to install active gas collection and control systems. Compliance with this trigger value can be estimated using regulatory default models based on a first order LFG generation model or measured via field studies; however, none of the existing regulatory methodologies include aerobic oxidation of either CH₄ or HAPs in landfill cover soils.

In general, the predominant HAP species in landfill gas are volatile and semi-volatile organic compounds which are volatilized directly from waste materials, plus other species (such as vinyl chloride) which can be produced during waste degradation via anaerobic microbial reactions. There is environmental concern with respect to net emissions of HAPs because some species can be hazardous to workers and adjacent inhabitants, some species such as benzene and vinyl chloride are known carcinogens, and other species can adversely affect air quality (for example, chlorofluorocarbons [CFCs] contribute to ozone depletion in the upper atmosphere (Rowland and Molina, 1974).

Several laboratory and field studies (Kightley et al., 1995; Czepiel et al. 1996; Bogner et al., 1997a,b; Liptay et al., 1998; Chanton et al., 1999; Christophersen et al., 2000, 2001; Scheutz et al., 2003a-c) have documented that landfill cover soils exposed to CH₄ can develop high capacities for CH₄ oxidation by indigenous methanotrophic microorganisms. Critical variables include soil texture and moisture content, temperature, CH₄ and O₂ concentrations, and nutrients (Whalen et al., 1990; Börgesson et al., 1998; Boeckx and Van Cleemput, 1996; DeVisscher et al., 1999; Hilger et al., 2000; Scheutz and Kjeldsen, 2003). Landfill "biocovers" engineered to optimize CH₄ oxidation have also been developed (Humer and Lechner, 1999, 2001, 2003). Because of the broad substrate specificity of the methane monooxygenase (MMO) enzyme, methanotrophs can also co-metabolize a variety of aliphatic compounds, including some halogenated hydrocarbons. However, there have been very few studies addressing either oxidation rates or net emissions of non-methane hydrocarbons in landfill settings. Kjeldsen et al. (1997) showed co-metabolic degradation of trichloroethylene and 1,1,1-trichloroethane in the presence of CH₄ in landfill gas-affected soils. Bogner et al. (1997c) measured very low emissions (10⁻⁶ to 10⁻⁴ g m⁻² d⁻¹) for selected NMOC species at a northeastern Illinois landfill under "worst case" conditions (thin interim soil cover over recently landfilled waste). The current paper provides an overview of field measurements and supporting laboratory studies at 2 French landfill sites; these studies provide the first complementary measurements of speciated HAP emissions in parallel with laboratory quantification of aerobic soil attenuation capacities. For additional details, readers should consult Bogner et al., 2003; Scheutz et al., 2003a-c).

FIELD SITES

Lapouyade is located near Bordeaux in southwestern France. The Phase I area received more than 300,000 tonnes of waste from 1996-1998. Final cover was placed in 1998 and consists of 40 cm coarse sand overlain by 80 cm of clayey silt and topsoil. This area was fully vegetated during the field campaign in September, 2001, but the upper 35 cm were very dry with a water content below 6.5% (w/w). The Phase II area was initiated in 1998; this area includes the current operational zone and a temporary cover zone where the refuse is overlain by 40 cm coarse sand. We also included a forested area immediately outside of the landfill as a control.

Grand'Landes is located in western France near Nantes. This 26 ha landfill has been accepting approximately 185,000 tonnes waste yr⁻¹ since 1989. The field campaign in September, 2002, focused on two experimental cells, 25A and 25B. Each cell had a surface area of 10,000 m²; 25A contained 69,000 m³ of waste and 25B contained 59,000 m³. Cell 25A has 5 conventional vertical wells and a cover design consisting of a coarse-grained leveling layer overlain by compacted clay and topsoil (total cover thickness approximately 1 m above the leveling layer). Cell 25B has an innovative gas collection system consisting of two horizontal perforated pipes within a 30 cm gravel gas collection layer. The two pipes are placed perpendicular to each other with a common collection point at one corner of the cell. The collection layer is overlain, in turn, by a geotextile layer, a 1.5 mm thick geomembrane, a second geotextile layer, 70 cm compacted clay, and 30 cm topsoil. Both cells 25A and 25B are vegetated. A grassy field on the landfill property functioned as our non-landfill control.

Herein we report on emission measurements conducted at Lapouyade at four locations on the fully vegetated Phase I final cover area (LP1, LP2, LP4, and LP6); one location on the Phase II temporary cover area (location LP5); and the forest control area (LP3). For Grand'Landes, we report on a subset of the emissions measurements conducted there, including area 25B with the geomembrane (F3); area 25A with conventional soil cover (F5, F7, F8, and F9); and the field control area.

It should be emphasized that the speciated HAP measurements were conducted in parallel with an extensive field campaign to quantify the CH₄ balance for selected cells with differing construction and gas management practices. These studies quantified the partitioning (mass time⁻¹) of the CH₄ generated into recovered, emitted, oxidized, migrated, and stored fractions (Bogner and Spokas, 1993), as summarized by Morcet et al. (2003) and previous papers referenced therein. The field studies at Lapouyade and Grand'Landes were collaborations among French, Danish, and U.S. research groups.

METHODS

Measurements at both sites included 1) CH₄, CO₂, and speciated HAP emissions using stainless steel static closed chambers; 2) CH₄ oxidation using a stable carbon isotopic technique on the emitted CH₄ (Chanton and Liptay papers), 3) soil gas profiles using customized stainless steel probes, and 4) the aerobic attenuation capacity of cover soils using laboratory batch incubations of soils collected at the same locations as the chamber and profile measurements. Appendix A and recent publications (Bogner et al., 2003; Scheutz et al., 2003a-c) give additional details on the field and laboratory methods.

RESULTS AND DISCUSSION

Source gas composition

Table 1 gives source gas composition and comparative fluxes for CH₄, CO₂, and NMOC species at Lapouyade; Table 2 summarizes results from Grand'Landes. The composite landfill gas in the collection header at Lapouyade averaged 49% CH₄ while the source gas at Grand'Landes averaged 33 V% CH₄; both sites had some air intrusion. The target species were all detected and quantified in the source gas at both Lapouyade and Grand'Landes. Toluene, xylenes, ethylbenzene, n-nonane, n-decane, perchloroethylene, and dichloromethane exhibited the highest concentrations (>10 µg L⁻¹) at Lapouyade. N-nonane and n-decane were elevated in the 25A header at Grand'Landes, and selected aromatics were elevated in both 25A and 25B headers. In general, the speciated HAPs in the source gas tended to be lower than reported by Brosseau and Heitz (1994) and values for seven codisposal landfills in the UK receiving both municipal waste and hazardous waste, as reported by Allen et al. (1997). The data were reasonably comparable to source gas values from Eklund et al. (1998) for the Fresh Kills Landfill, New York, USA.

Methane and speciated NMOC emissions

Source gas concentrations and emissions of CH₄ and HAP species from the final cover, temporary cover, and adjacent forest area (control) at Lapouyade are shown in Table 1. Observed CH₄ fluxes from the final cover area varied between -0.01 and 0.008 g·m⁻²·d⁻¹; however, LP6 was a hot spot with high CH₄ flux (10.0 g m⁻² d⁻¹). The negative fluxes (LP2 and LP4) indicate oxidation of atmospheric CH₄ with no landfill CH₄ emissions, as reported in previous field studies (Bogner et al., 1995, 1997b, 1999; Börjesson and Svensson, 1997). In a parallel field investigation by French investigators at Lapouyade using dynamic flux chambers placed randomly on the final cover area, the average CH₄ flux from the finished cell was 1.97±0.88 g m⁻² d⁻¹ with hot spots exhibiting high fluxes of 3.7-16.2 g m⁻² d⁻¹; for the temporary cover cell, CH₄ emissions were higher, averaging 37.8±14 g m⁻² d⁻¹ with a maximum flux of 78.2 g m⁻² d⁻¹. Using a stable carbon isotopic method described in previous publications (Liptay et al., 1998; Chanton et al., 1999; Chanton and Liptay, 2000), the fractional CH₄ oxidation ranged from 7-34% for the final cover cell and 5% for the temporary cover cell. Due to differences in CH₄ flux from the anaerobic zone, design of cover soils and CH₄ oxidation rates, a wide range of CH₄ emission rates have been reported in the literature for landfill settings, varying between 0.0004 and 4000 g m⁻² d⁻¹ with negative emissions also possible (Bogner et al.,

**TABLE 1 – SOURCE GAS CONCENTRATIONS ($\mu\text{g L}^{-1}$) AND SURFACE EMISSIONS ($\text{g m}^{-2} \text{d}^{-1}$)
AT LAPOUYADE LANDFILL. FC=FINAL COVER; TC=TEMPORARY COVER.**

	Chemical formula	Source gas conc. $\mu\text{g}\cdot\text{L}^{-1}$	LP1 Flux $\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$	LP2 Flux $\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$	LP4 Flux $\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$	LP6 Flux $\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$	LP5 Flux $\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$	LP3 Flux $\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$
Location			FC	FC	FC	FC	TC	Forest-control
Methane	CH ₄	48.5% v/v	0.0084	-0,0095	-0,0104	10.0	49.9	-0.0033
Carbon dioxide	CO ₂	33.7% v/v	8.0	13.1	15.6	77.3	107.4	19.3
Oxidation (%)*			8.5	6.6	12.3	33.5	5.1	ND**
Alkanes								
Ethane	C ₂ H ₆	1.5	1.42·10 ⁻⁶	6.94·10 ⁻⁶	4.69·10 ⁻⁶	2.13·10 ⁻⁵	1.60·10 ⁻⁴	8.60·10 ⁻⁷
Propane	C ₃ H ₈	2.6	-6.45·10 ⁻⁵	1.74·10 ⁻⁵	7.91·10 ⁻⁶	5.87·10 ⁻⁵	7.36·10 ⁻⁵	2.48·10 ⁻⁶
n-Butane	C ₄ H ₁₀	5.5	-1.45·10 ⁻⁴	7.18·10 ⁻⁶	3.47·10 ⁻⁶	1.72·10 ⁻⁵	1.69·10 ⁻⁴	-1.64·10 ⁻⁷
n-Pentane	C ₅ H ₁₂	1.7	-3.64·10 ⁻⁶	1.03·10 ⁻⁵	1.42·10 ⁻⁵	7.74·10 ⁻⁶	7.04·10 ⁻⁵	5.55·10 ⁻⁷
n-Hexane	C ₆ H ₁₄	0.8	6.26·10 ⁻⁷	2.68·10 ⁻⁶	2.60·10 ⁻⁶	1.40·10 ⁻⁶	6.55·10 ⁻⁵	3.74·10 ⁻⁸
n-Heptane	C ₇ H ₁₆	1.2	-2.91·10 ⁻⁶	1.21·10 ⁻⁶	1.66·10 ⁻⁶	-9.75·10 ⁻⁶	4.33·10 ⁻⁴	-7.60·10 ⁻⁸
n-Octane	C ₈ H ₁₈	0.7	-1.66·10 ⁻⁶	7.00·10 ⁻⁸	8.44·10 ⁻⁷	-9.44·10 ⁻⁶	2.34·10 ⁻⁴	BDL***
n-Nonane	C ₉ H ₂₀	28.1	-1.47·10 ⁻⁵	-7.86·10 ⁻⁸	-8.87·10 ⁻⁷	-2.56·10 ⁻⁵	8.14·10 ⁻⁵	-3.06·10 ⁻⁷
n-Decane	C ₁₀ H ₂₂	11.2	-7.18·10 ⁻⁵	3.49·10 ⁻⁷	-1.94·10 ⁻⁶	-3.19·10 ⁻⁵	3.21·10 ⁻⁵	-1.23·10 ⁻⁷
i-Butane	C ₄ H ₁₀	5.0	-1.15·10 ⁻⁴	5.79·10 ⁻⁶	3.00·10 ⁻⁶	3.70·10 ⁻⁵	1.18·10 ⁻⁴	2.02·10 ⁻⁷
i-Pentane	C ₅ H ₁₂	7.0	-2.57·10 ⁻⁵	3.39·10 ⁻⁶	3.51·10 ⁻⁶	1.91·10 ⁻⁵	2.23·10 ⁻⁴	7.82·10 ⁻⁸
2-methylpentane	C ₆ H ₁₄	3.0	BDL	BDL	BDL	1.19·10 ⁻⁶	BDL	-3.08·10 ⁻⁷
3-methylpentane	C ₆ H ₁₄	1.0	-9.33·10 ⁻⁷	BDL	BDL	1.78·10 ⁻⁷	BDL	-2.33·10 ⁻⁷
Alkenes								
Ethene	C ₂ H ₄	5.2	1.04·10 ⁻⁵	2.92·10 ⁻⁶	1.84·10 ⁻⁵	5.19·10 ⁻⁶	1.68·10 ⁻⁵	-2.28·10 ⁻⁸
Propene	C ₃ H ₆	5.5	7.19·10 ⁻⁷	5.37·10 ⁻⁶	3.65·10 ⁻⁶	-3.85·10 ⁻⁶	1.72·10 ⁻⁴	-5.26·10 ⁻⁸
t-2-Butene	C ₄ H ₈	0.8	-1.94·10 ⁻⁷	1.19·10 ⁻⁶	BDL	BDL	2.42·10 ⁻⁵	BDL
1-Butene	C ₄ H ₈	0.3	-6.01·10 ⁻⁷	1.99·10 ⁻⁶	5.92·10 ⁻⁸	1.59·10 ⁻⁶	5.35·10 ⁻⁵	-3.65·10 ⁻⁸
i-Butene	C ₄ H ₈	2.7	3.16·10 ⁻⁶	9.44·10 ⁻⁶	1.20·10 ⁻⁶	-7.15·10 ⁻⁷	7.96·10 ⁻⁵	3.04·10 ⁻⁷
c-2-Butene	C ₄ H ₈	0.4	-2.67·10 ⁻⁸	5.33·10 ⁻⁷	BDL	-4.56·10 ⁻⁷	1.84·10 ⁻⁵	BDL
Isoprene	C ₅ H ₈	0.4	4.86·10 ⁻⁷	1.08·10 ⁻⁶	-3.27·10 ⁻⁷	-1.34·10 ⁻⁶	1.54·10 ⁻⁵	-3.23·10 ⁻⁶
Ethyne	C ₂ H ₂	0.6	-1.08·10 ⁻⁷	-6.34·10 ⁻⁷	1.34·10 ⁻⁷	-3.50E-07	-4.65·10 ⁻⁷	-3.89·10 ⁻⁷
Halogenated hydrocarbons								
CFC-11	CCl ₃ F	2.0	-7.92·10 ⁻⁵	5.18·10 ⁻⁶	2.24·10 ⁻⁶	7.63·10 ⁻⁵	2.08·10 ⁻⁵	5.21·10 ⁻⁷
CFC-12	CCl ₂ F ₂	5.7	-1.68·10 ⁻⁵	2.17·10 ⁻⁶	1.84·10 ⁻⁷	1.04·10 ⁻⁵	2.56·10 ⁻⁵	-7.86·10 ⁻⁸
HCFC-22	CHClF ₂	0.0	-4.89·10 ⁻⁶	5.03·10 ⁻⁷	-4.06·10 ⁻⁸	2.26·10 ⁻⁵	5.74·10 ⁻⁵	-1.50·10 ⁻⁷
H-1211	CBrClF ₂	0.8	-5.90·10 ⁻⁵	BDL	BDL	BDL	BDL	BDL
Trichloromethane	CHCl ₃	0.0	4.26·10 ⁻⁷	6.58·10 ⁻⁷	7.84·10 ⁻⁷	4.56·10 ⁻⁶	1.02·10 ⁻⁶	7.56·10 ⁻⁶
Dichloromethane	CH ₂ Cl ₂	10.3	-2.10·10 ⁻⁵	2.08·10 ⁻⁷	4.98·10 ⁻⁸	-1.06·10 ⁻⁵	-3.22·10 ⁻⁷	BDL
Chloromethane	CH ₃ Cl	0.1	-2.24·10 ⁻⁶	-4.98·10 ⁻⁷	1.64·10 ⁻⁶	-3.90·10 ⁻⁶	-2.04·10 ⁻⁶	-3.05·10 ⁻⁶
Perchloroethylene	C ₂ Cl ₄	47.4	-2.37·10 ⁻⁷	1.37·10 ⁻⁶	1.75·10 ⁻⁷	2.03·10 ⁻⁶	2.30·10 ⁻⁵	7.19·10 ⁻⁸
Trichloroethylene	C ₂ HCl ₃	0.8	BDL	BDL	BDL	-1.08·10 ⁻⁶	BDL	BDL
Vinyl chloride	C ₂ H ₃ Cl	2.4	BDL	BDL	BDL	-1.03·10 ⁻⁶	1.03·10 ⁻⁵	BDL
Aromatics								
Benzene	C ₆ H ₆	1.8	5.67·10 ⁻⁷	5.14·10 ⁻⁷	2.25·10 ⁻⁷	-3.92·10 ⁻⁶	3.41·10 ⁻⁵	-2.88·10 ⁻⁷
Toluene	C ₇ H ₈	76.8	6.97·10 ⁻⁶	5.56·10 ⁻⁶	1.03·10 ⁻⁶	-3.57·10 ⁻⁵	-2.18·10 ⁻⁵	-3.20·10 ⁻⁷
Ethylbenzene	C ₈ H ₁₀	24.8	6.70·10 ⁻⁷	2.75·10 ⁻⁶	-1.05·10 ⁻⁶	-2.78·10 ⁻⁵	-6.96·10 ⁻⁵	-1.38·10 ⁻⁷
Xylene (m,p,o)	C ₈ H ₁₀	85.5	1.24·10 ⁻⁵	1.45·10 ⁻⁵	2.8·10 ⁻⁶	-3.24·10 ⁻⁵	3.71·10 ⁻⁴	1.28·10 ⁻⁶

*Determined by isotopic analysis of the emitted CH₄ (Liptay et al., 1998; Chanton et al., 1999; Chanton and Liptay, 2000) **ND=not determined or not applicable.

***BDL = below detection limit (20 pptv for most species).

1997a). The CO₂ fluxes at Lapouyade using an opaque chamber quantified the dark respiration of the soil-plant community. The observed values ranged from similar to higher than natural soils; the high values were associated with hot spots (areas of high CH₄ flux). We suggest that the high CO₂ fluxes were a combination of increased soil respiration due to higher temperatures, oxidized landfill CH₄, and directly emitted landfill CO₂.

At Lapouyade, the speciated HAP fluxes from the final cover area were all very small with positive and negative fluxes on the order of 10⁻⁷ to 10⁻⁵ g m⁻² d⁻¹. Species with negative fluxes included aromatics, n-nonane, n-decane, ethyne, and methyl chloride. Previously, Bogner et al.(1997c) had also observed negative emissions for selected aromatics. The HAP flux rates in the forest control area were generally lower (order of 10⁻⁸ to 10⁻⁷ g m⁻² d⁻¹) and negative. Higher and mainly positive fluxes in the order of 10⁻⁵ to 10⁻⁴ g·m⁻²·day⁻¹ were obtained from the temporary cover area. In the previous Illinois study (Bogner et al., 1997c), emissions of most HAP species from an area with temporary cover (35 cm stony clay) were generally 10⁻⁵ to 10⁻³ g m⁻² d⁻¹, which is comparable to emissions from the temporary cover area (LP5) at Lapouyade.

Selected HAPs are also emitted naturally from soil surfaces and plants; for example, Fukui and Doskey (1998) measured isoprene emissions from a grassland site (4.3 10⁻⁵ g m⁻² d⁻¹) that were higher than the isoprene fluxes at Lapouyade. The natural emissions of volatile gaseous species from vegetation is currently an active area of research. It cannot be excluded that surface emissions of isoprene and selected other species at Lapouyade are from natural sources. In addition, some HAP species in the ambient air were elevated above observed levels in landfill gas [data not shown]. At the forest control station LP3, not affected by landfill gas, negative fluxes for benzene, toluene and ethylbenzene were measured. This was likely the result of elevated atmospheric concentrations of aromatics and other speciated HAPs above the soil surface at the forest site—either due to vehicular exhaust from the nearby road with heavy traffic from waste trucks or its downwind location from the active tipping area. Air samples downwind from the active cell had significantly greater CH₄ concentrations (17 to 36 ppmv) compared with upwind samples (1.92 ppmv). Moreover, air samples collected across the landfill before dawn under a nocturnal inversion had elevated CH₄ concentrations up to a maximum of 394 ppmv. Thus, it is not surprising that landfill cover soils can function both as sources *and* sinks for atmospheric CH₄ and HAP species. In general, because of the temporal and spatial dynamics of small HAP fluxes from landfill, atmospheric, and vegetation sources in cells with various gas control strategies, it is very important to understand source/sink relationships for individual species and chemically-similar groups.

The results from Grand'Landes are summarized in Table 2. Both cells (25A and 25B) had active gas recovery. The CH₄ fluxes from a 6-point static chamber transect across cell 25B were all negative, ranging from -0.2 to -2.2 mg m⁻² d⁻¹. [Data not shown.] Methane was thus being oxidized out of the atmosphere by methanotrophic microorganisms in the soil above the geomembrane. Five of the six fluxes from a similar transect across cell 25A also resulted in a narrow range of negative fluxes from -0.3 to -2.4 mg m⁻² d⁻¹; one flux was essentially zero (time plot resulted in a horizontal line). Flux F9 (Table 2) was the highest CH₄ flux observed among known hot spots identified by French colleagues in dynamic chamber tests being conducted as part of the same field campaign; their mean values were 0.001 (25A; n=42) and 0.62 (25B, n=75) g m⁻² d⁻¹ (Baroudi and Jodart, 2003).

Speciated HAP fluxes at Grand'Landes (Table 2) were similar to observed ranges at Lapouyade with positive and negative fluxes on the order of 10⁻⁸ to 10⁻⁶ g m⁻² d⁻¹. The highest positive fluxes on the two cells were observed for ethene (10⁻⁵ g m⁻² d⁻¹), but these were exceeded by the ethene flux from the control area, suggesting a natural source. At the F9 hot spot, the highest positive flux was for i-pentane at 2.1 X 10⁻⁴ g m⁻² d⁻¹. In general, the positive fluxes at F9 were in a higher range of 10⁻⁷ to 10⁻⁴ compared to the F3, F5, F7, and F8 fluxes. Fluxes of aromatics from both the landfill cells and the control area, but not the hot spot, were predominately negative, consistent with the discussion above for Lapouyade.

**TABLE 2 - SOURCE GAS CONCENTRATIONS ($\mu\text{g L}^{-1}$) AND SURFACE EMISSIONS ($\text{g m}^{-2} \text{d}^{-1}$)
AT GRAND'LANDES LANDFILL. FC=FINAL COVER; TC=TEMPORARY COVER.**

	25A Source Gas Conc. $\mu\text{g}\cdot\text{L}^{-1}$	25B Source Gas Conc. $\mu\text{g}\cdot\text{L}^{-1}$	25B-F3 Flux $\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$	25A-F5 Flux $\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$	25A-F7 Flux $\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$	25A-F8 Flux $\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$	25A-F9 Flux $\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$	Control $\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$
Cover			FC,geomemb	FC,soil	FC, soil	FC, soil	edge/hotspot	Field control
Methane	37.5 % v/v	29.1 % v/v	-0.0022	0.0	-0.0011	0.0001	29.0	4.8
Carbon dioxide	25.1 % v/v	25.0 % v/v						
Oxidation (%)*			ND	ND	ND	ND	7.1	ND
Alkanes								
Ethane	2.3	2.06	$3.73\cdot 10^{-6}$	$3.45\cdot 10^{-6}$	$4.64\cdot 10^{-6}$	$4.11\cdot 10^{-6}$	$3.22\cdot 10^{-5}$	$8.99\cdot 10^{-6}$
Propane	3.48	2.7	$-3.03\cdot 10^{-6}$	$2.33\cdot 10^{-6}$	$2.08\cdot 10^{-6}$	$3.92\cdot 10^{-6}$	$5.98\cdot 10^{-5}$	$5.24\cdot 10^{-6}$
n-Butane	6.21	3.94	$-2.39\cdot 10^{-6}$	$1.73\cdot 10^{-6}$	$7.77\cdot 10^{-7}$	$2.53\cdot 10^{-6}$	$4.73\cdot 10^{-5}$	$2.15\cdot 10^{-6}$
n-Pentane	1.73	3.26	$7.77\cdot 10^{-6}$	$6.23\cdot 10^{-6}$	$6.19\cdot 10^{-6}$	$5.77\cdot 10^{-6}$	$3.47\cdot 10^{-5}$	$1.28\cdot 10^{-5}$
n-Hexane	0.75	0.67	$1.76\cdot 10^{-7}$	$1.18\cdot 10^{-6}$	$4.80\cdot 10^{-7}$	0.00	$2.03\cdot 10^{-6}$	$1.19\cdot 10^{-6}$
n-Heptane	5.27	3.75	$-3.92\cdot 10^{-7}$	$-1.41\cdot 10^{-7}$	$-1.30\cdot 10^{-7}$	$-5.87\cdot 10^{-6}$	$3.44\cdot 10^{-7}$	$1.21\cdot 10^{-6}$
n-Octane	3.51	1.21	$-4.76\cdot 10^{-7}$	$-1.16\cdot 10^{-7}$	$-9.55\cdot 10^{-8}$	$-3.30\cdot 10^{-6}$	$1.01\cdot 10^{-5}$	$-1.01\cdot 10^{-6}$
n-Nonane	10.60	2.37	$-1.20\cdot 10^{-5}$	$9.31\cdot 10^{-6}$	$1.19\cdot 10^{-8}$	$-2.68\cdot 10^{-5}$	$2.71\cdot 10^{-7}$	$-8.69\cdot 10^{-6}$
n-Decane	16.27	2.74	$-4.71\cdot 10^{-6}$	$-2.56\cdot 10^{-7}$	$-1.27\cdot 10^{-5}$	$-3.76\cdot 10^{-4}$	$1.63\cdot 10^{-5}$	$-1.94\cdot 10^{-5}$
i-Butane	5.02	2.96	$3.11\cdot 10^{-7}$	$1.88\cdot 10^{-6}$	$1.84\cdot 10^{-7}$	$-1.10\cdot 10^{-6}$	$7.29\cdot 10^{-5}$	$6.69\cdot 10^{-7}$
i-Pentane	3.94	8.19	$-1.23\cdot 10^{-7}$	$5.14\cdot 10^{-7}$	$4.22\cdot 10^{-7}$	$-1.71\cdot 10^{-6}$	$2.11\cdot 10^{-4}$	$1.15\cdot 10^{-6}$
2-methylpentane	1.5	1.76	$2.20\cdot 10^{-8}$	$2.70\cdot 10^{-7}$	$2.24\cdot 10^{-7}$	$1.59\cdot 10^{-8}$	$5.00\cdot 10^{-6}$	$4.22\cdot 10^{-7}$
3-methylpentane	0.81	0.99	$-2.13\cdot 10^{-7}$	$2.70\cdot 10^{-8}$	$1.60\cdot 10^{-8}$	$-3.50\cdot 10^{-7}$	$7.72\cdot 10^{-6}$	$1.33\cdot 10^{-7}$
Alkenes								
Ethene	2.76	1.74	$4.80\cdot 10^{-5}$	$7.35\cdot 10^{-5}$	$3.50\cdot 10^{-5}$	$2.84\cdot 10^{-5}$	$6.87\cdot 10^{-6}$	$1.99\cdot 10^{-4}$
Propene	7.77	5.00	$2.24\cdot 10^{-5}$	$3.56\cdot 10^{-6}$	$1.62\cdot 10^{-6}$	$3.05\cdot 10^{-6}$	$9.25\cdot 10^{-6}$	$4.22\cdot 10^{-6}$
t-2-Butene	0.26	0.24	$-7.68\cdot 10^{-7}$	$2.20\cdot 10^{-8}$	$4.69\cdot 10^{-8}$	$-1.82\cdot 10^{-6}$	$1.56\cdot 10^{-6}$	$2.27\cdot 10^{-7}$
1-Butene	0.25	0.24	$-5.53\cdot 10^{-7}$	$-6.46\cdot 10^{-7}$	$2.50\cdot 10^{-7}$	$-5.74\cdot 10^{-7}$	$4.91\cdot 10^{-6}$	$6.70\cdot 10^{-7}$
i-Butene	0.29	0.42	$1.42\cdot 10^{-6}$	$-3.25\cdot 10^{-7}$	$1.05\cdot 10^{-6}$	$5.64\cdot 10^{-7}$	$7.40\cdot 10^{-6}$	$3.28\cdot 10^{-6}$
c-2-Butene	0.25	0.20	$-5.49\cdot 10^{-7}$	$-8.79\cdot 10^{-8}$	$5.21\cdot 10^{-8}$	$-2.27\cdot 10^{-6}$	$1.03\cdot 10^{-6}$	$1.69\cdot 10^{-7}$
Isoprene	0.17	0.11	$4.11\cdot 10^{-7}$	$5.39\cdot 10^{-7}$	$4.30\cdot 10^{-7}$	$6.16\cdot 10^{-6}$	$-2.22\cdot 10^{-7}$	$-4.27\cdot 10^{-7}$
Ethyne	0.17	0.11	$6.84\cdot 10^{-7}$	$5.12\cdot 10^{-7}$	$-3.99\cdot 10^{-7}$	$-3.14\cdot 10^{-8}$	$-1.78\cdot 10^{-6}$	$6.56\cdot 10^{-7}$
Halogenated hydrocarbons								
CFC-11	3.05	1.62	$6.54\cdot 10^{-7}$	$3.73\cdot 10^{-5}$	$1.33\cdot 10^{-6}$	$7.86\cdot 10^{-7}$	$4.36\cdot 10^{-7}$	$2.66\cdot 10^{-6}$
CFC-12	0.67	4.90	$-2.16\cdot 10^{-7}$	$-2.27\cdot 10^{-7}$	$5.39\cdot 10^{-7}$	$6.02\cdot 10^{-7}$	$-2.13\cdot 10^{-8}$	$-1.56\cdot 10^{-7}$
HCFC-22	1.84	1.25	$-1.54\cdot 10^{-7}$	$-6.10\cdot 10^{-8}$	$1.85\cdot 10^{-7}$	$-2.39\cdot 10^{-8}$	$4.64\cdot 10^{-6}$	$-5.20\cdot 10^{-8}$
H-1211	BDL	BDL	$-8.44\cdot 10^{-9}$	$-3.89\cdot 10^{-9}$	$4.61\cdot 10^{-9}$	$-3.05\cdot 10^{-9}$	$4.37\cdot 10^{-9}$	$2.84\cdot 10^{-9}$
Trichloromethane	BDL	0.02	$-5.03\cdot 10^{-6}$	$3.14\cdot 10^{-5}$	$4.46\cdot 10^{-5}$	$1.80\cdot 10^{-5}$	$-1.29\cdot 10^{-6}$	$-6.15\cdot 10^{-6}$
Dichloromethane	0.18	0.41	$-2.75\cdot 10^{-7}$	$-3.13\cdot 10^{-7}$	$-2.60\cdot 10^{-7}$	$-6.74\cdot 10^{-7}$	$-8.53\cdot 10^{-7}$	$-6.42\cdot 10^{-7}$
Chloromethane	0.57	0.69	$-8.08\cdot 10^{-7}$	$3.37\cdot 10^{-7}$	$-4.41\cdot 10^{-7}$	$-2.36\cdot 10^{-6}$	$2.64\cdot 10^{-7}$	$-2.71\cdot 10^{-7}$
Perchloroethylene	1.65	0.63	$-1.41\cdot 10^{-7}$	$-6.24\cdot 10^{-7}$	$1.85\cdot 10^{-7}$	$1.38\cdot 10^{-7}$	$4.38\cdot 10^{-7}$	$3.85\cdot 10^{-7}$
Trichloroethylene	0.19	0.10	$-2.24\cdot 10^{-9}$	$1.85\cdot 10^{-8}$	$-4.76\cdot 10^{-8}$	$-4.30\cdot 10^{-7}$	$4.02\cdot 10^{-7}$	$1.32\cdot 10^{-7}$
Aromatics								
Benzene	0.74	0.30	$-1.43\cdot 10^{-6}$	$-8.87\cdot 10^{-7}$	$-2.03\cdot 10^{-7}$	$-1.53\cdot 10^{-6}$	$8.26\cdot 10^{-8}$	$-7.38\cdot 10^{-8}$
Toluene	20.59	6.87	$-5.71\cdot 10^{-6}$	$-1.43\cdot 10^{-6}$	$-3.24\cdot 10^{-6}$	$-4.68\cdot 10^{-5}$	$-1.69\cdot 10^{-6}$	$4.05\cdot 10^{-6}$
Ethylbenzene	33.8	13.49	$-2.16\cdot 10^{-6}$	$-3.08\cdot 10^{-7}$	$-3.33\cdot 10^{-6}$	$-8.56\cdot 10^{-5}$	$5.92\cdot 10^{-6}$	$-3.31\cdot 10^{-6}$
Xylene (m,p,o)	52.84	15.47	$-6.76\cdot 10^{-6}$	$-9.48\cdot 10^{-7}$	$-3.27\cdot 10^{-5}$	$-4.05\cdot 10^{-4}$	$3.37\cdot 10^{-5}$	$-3.26\cdot 10^{-5}$

See notes on Table 1.

Soil gas concentration profiles

Soil gas concentration profiles are influenced by numerous microbial, gaseous transport, and meteorological processes. If we compare three soil gas profiles from the final cover area (LP1, LP2 and LP6) and one from the temporary cover area (LP5) at Lapouyade, one can observe significant differences in concentrations among HAP species but similar trends among chemically related compounds at the same location. This is especially true for the aromatics and the alkanes. Most HAP species increased in concentration over several orders of magnitude from the ground surface to the top of refuse. However, some species (e.g., PCE, TCM, CFC-12) had relatively constant soil gas concentrations with depth, while others (aromatics) showed increasing gas concentrations toward the surface, consistent with the atmospheric uptake often observed for individual aromatics. Figure 1 shows soil gas profiles for major gases and selected HAPs at location LP6 (final cover) at Lapouyade. At 80 cm, the soil was fully anaerobic with high concentrations of CH_4 and CO_2 . Between 80 and 60 cm, the shift in CH_4 and CO_2 concentrations and the increase in C^{13} - CH_4 together with the decrease in C^{13} - CO_2 indicates CH_4 oxidation. Note that all of the aromatics and vinyl chloride show a similar trend at 60-80 cm depth. These compounds may be readily degraded under aerobic conditions.

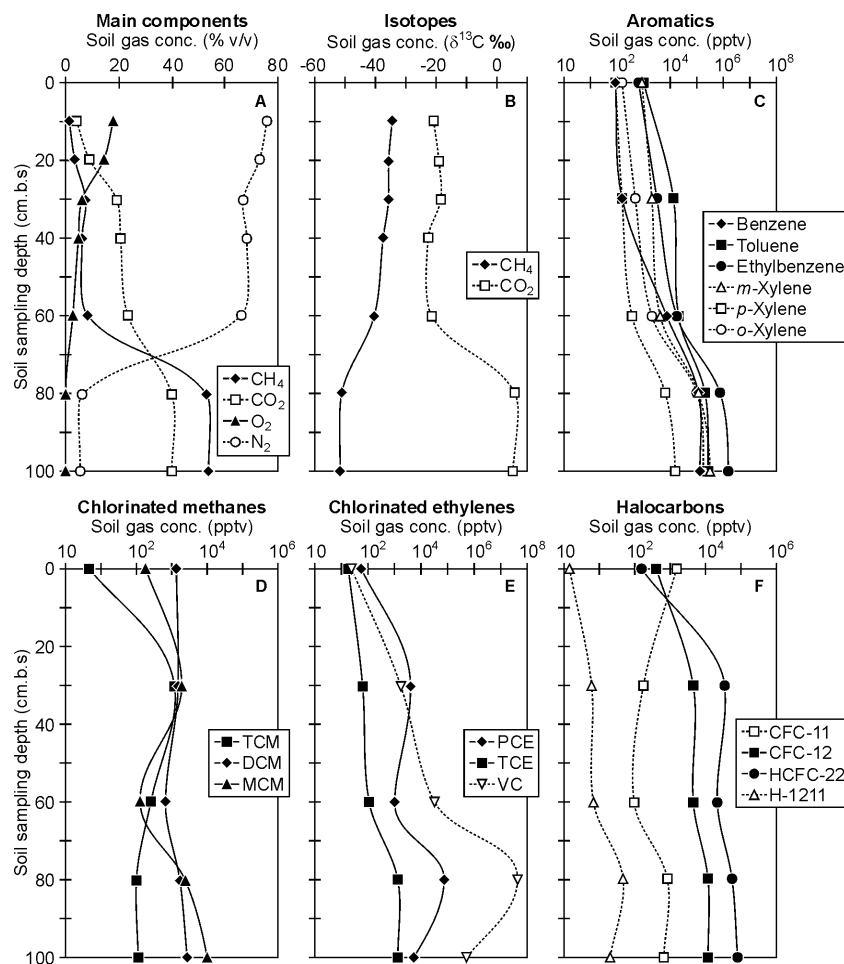


FIGURE 1. SOIL GAS CONCENTRATION PROFILES AT LP6 (FINAL COVER AREA AT LAPOUYADE).

Laboratory Batch Incubation Studies: Degradation Capacity of Landfill Soils

All batch studies showed declining CH₄ and O₂ in parallel in increasing CO₂. Because there were no lag phases, CH₄ oxidation was occurring by well-adapted microorganisms; in contrast, no CH₄ oxidation occurred in the sterilized controls. The oxidation kinetics were examined by plotting concentration vs. time. Neither CH₄ nor O₂ was limiting in these experiments, resulting in zero-order kinetics for CH₄ oxidation. In some cases, decreasing concentrations of HAPs toward the end of the experimental period limited oxidation rates, and kinetics became first-order. In order to compare among different compounds, maximum rates were calculated by applying zero order kinetics to the data from the starting point (t=0) to the point at which degradation was 90% complete (t when C/C₀ = 90%).

At experimental conditions (see Appendix A), the maximum CH₄ oxidation rates were 35 μg g dry soil⁻¹ d⁻¹ at Lapouyade and 674 μg g dry soil⁻¹ d⁻¹ at Grand'Landes. With respect to the speciated HAPs, the highest oxidation rates were observed for the aromatics at Lapouyade (benzene=27.9; toluene=38.7 μg g dry soil⁻¹ d⁻¹) and dichloromethane at Grand'Landes (11.2 μg g dry soil⁻¹ d⁻¹). At Grand'Landes, the maximum oxidation rates for benzene and toluene were approximately 2-3 μg g dry soil⁻¹ d⁻¹, or about an order of magnitude less than Lapouyade. Figure 2 shows relative headspace concentrations of speciated HAPs in batch experiments from Lapouyade. Note that the aromatics and lower chlorinated compounds were degraded, with decreasing rates corresponding to more chlorine atoms in the molecule; fully chlorinated compounds (PCE, CFCs) were recalcitrant. There are a large number of microorganisms that can aerobically degrade benzene and toluene; some aerobic microorganisms can also degrade chlorinated compounds via co-oxidation mechanisms. With respect to depth-based tests, the maximum oxidation activity for CH₄ and HAPs was observed at 50 cm at Lapouyade with a secondary maximum for benzene and toluene at 20 cm. For Grand'Landes, the maximum oxidation activity for both CH₄ and aromatics occurred at about 5-10 cm below the surface. However, at both sites a relatively thick oxidation zone was observed (25-50 cm), and the zone of optimum activity would be expected to vary temporally with changing temperature, soil moisture, and gaseous transport of CH₄ and HAPs.

CONCLUSIONS

Based on the emission measurements discussed above and complementary laboratory experiments documenting the oxidation capacity and kinetics of landfill soils (Scheutz et al., 2003a-c), a general coherence was observed between emissions and biodegradability of individual HAP species. The emissions consisted mainly of compounds which are not degradable or slowly degraded under aerobic conditions (e.g., CFCs and higher chlorinated compounds), while low to negative emissions were observed for compounds which are readily degradable under aerobic conditions: especially the aromatics and lower chlorinated compounds. The general conclusions of this work are as follows:

1. In general, speciated HAP emissions from landfill cover soils are extremely low as shown in Tables 1-2, with flux rates for some species overlapping with ranges for natural background/control areas.
2. High oxidation capacities can develop in landfill soils for both methane and selected HAPs (especially aromatics and lower chlorinated compounds). This capacity for oxidation effectively limits the emissions of HAPs from landfills to the atmosphere.
3. Both positive (+) emissions (soil to atmosphere) and negative (-) emissions (uptake from atmosphere) are possible, due to the aerobic oxidation capacity of landfill cover soils and transport of individual gaseous species into cover soils from either landfill sources below or atmospheric sources above. It is thus important to recognize the bidirectional nature of gaseous fluxes through landfill cover soils.
4. Techniques to measure fluxes must be able to measure bidirectional fluxes of individual species. At present, static chambers are the only technique that can quantify both (+) and (-) fluxes. Moreover, use of analytical techniques which measure the total non-methane organic compounds in emitted landfill gas (e.g., method 25c for total NMOCs) is not recommended because individual species may be differentially elevated in either the source gas or the atmosphere, yielding misleading information on fluxes.

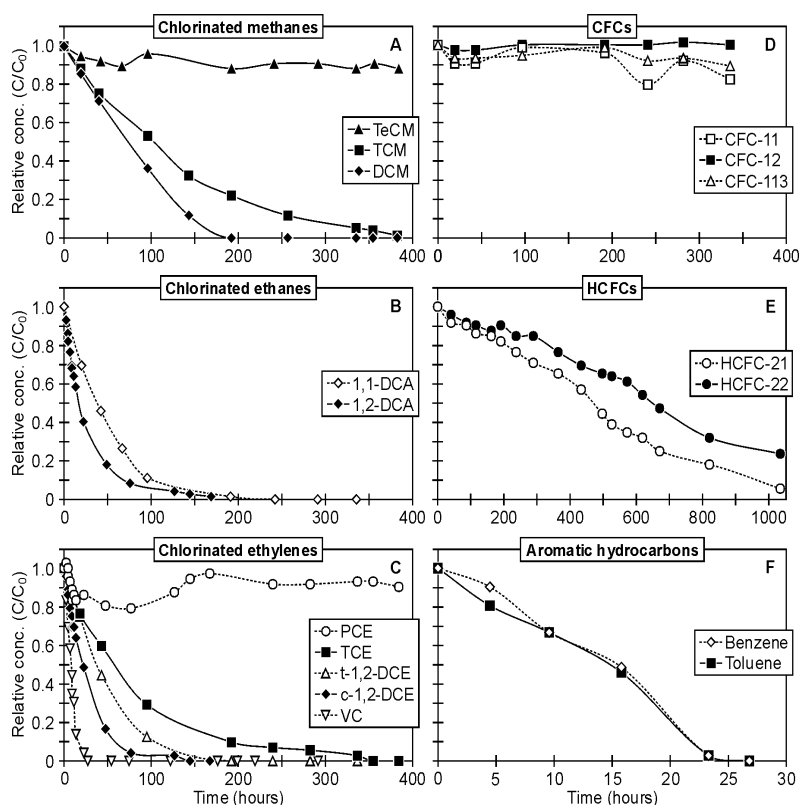


FIGURE 2. RELATIVE HEADSPACE CONCENTRATIONS FOR SPECIATED HAPS IN BATCH EXPERIMENTS CONTAINING SOIL SAMPLED AT 35-45 CM DEPTH IN FINAL COVER AREA AT LAPOUYADE (LP6). CONCENTRATIONS NORMALIZED TO INITIAL CONCENTRATION (AT T=0). A. CHLORINATED METHANES. B. CHLORINATED ETHANES. C. CHLORINATED ETHYLENES. D. CHLOROFLUOROCARBONS. E. HYDROCHLOROFLUOROCARBONS. F. AROMATICS. NOTE DIFFERENT TIME SCALES.

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Appendix A.

Supporting information on field and laboratory methods.

At both sites, emission rates of CH₄, CO₂, and speciated HAPs were measured using static flux chambers. At each measurement point, two circular iron collars functioned as bases for two static chambers (A and B). The collars were placed adjacent to each other at a depth of 4-5 cm in the cover soil and, during sampling periods of 20 minutes (CH₄, CO₂) or 120 minutes (speciated HAPs), each was topped by a chamber consisting of a stainless steel (SS) hemisphere that exactly fit a circular trough welded to the top of each collar. During monitoring periods, the trough was filled with distilled water and the chambers secured with hand clamps. Each chamber top was fitted with a single SS Swagelok sampling port for sampling using a gas-tight syringe [for CH₄ and CO₂] or direct connection to an evacuated 2 L electropolished canister [for speciated HAPs]. Chamber volume was 31830 cm³, and the enclosed surface area was 1217 cm² resulting in a volume/area ratio (cm³ cm⁻²) of 26.

Emission measurements for CH₄ and CO₂ relied on five gas samples of 25-50 mL withdrawn over 30 minutes using syringes and stored in pre-evacuated serum bottles. Based on the results of a pilot study conducted at Lapouyade in May, 2001, three 2 L stainless steel canister samples/test were taken for Speciated HAPs in a subsequent chamber test: the first sample was taken at time zero in chamber A; after 120 minutes an additional sample was taken in both chambers A and B. The fluxes reported herein rely on the initial value from chamber A and final value from chamber B (adjacent). The second 120 minute sample from chamber A acted as a maximum check on the observed flux from the adjacent chambers. Fluxes were calculated from the product of the change in concentration over time (dc/dt) and the [chamber volume/chamber area] ratio (Rolston, 1986). 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 minutes was tested at a location with relatively high CH₄ emissions (7.9 g m⁻² d⁻¹), the final data points indicated only a minor flattening of the dc/dt slope with $r^2 > 0.98$.

Following the flux measurements using chambers, soil gas profiles were determined at the same points via gas probes installed at different depths in the soil cover. We used stainless steel tubes (10 mm

ID) which were closed at the bottom and had slits at the lower 3 cm; these were hammered into the ground at depths of 10, 20, 30, 40, 60, 80, and 100-cm. Using gas-tight syringes, 25-50 mL samples for major gases (CH_4 , CO_2 , O_2 , and N_2) were withdrawn and stored in pre-evacuated glass serum bottles. For speciated HAPs, samples were taken thereafter at a maximum of four different depths (typically 30, 60, 80, and 100 cm). Samples were retained in pre-evacuated 2 L stainless steel canisters.

Concentrated source gas samples for both major gases and speciated HAPs were taken from the main header lines to the flare. Stable carbon isotopes ($\delta^{13}\text{C}$) were determined on CH_4 in the source gas, ambient air, soil gas profile samples, and the final (20-min.) chamber sample.

Major gases and stable carbon isotopes ($\delta^{13}\text{C}$) were analyzed at Florida State University. Methane and CO_2 concentrations below 1% were determined on a Shimadzu 14A gas chromatograph with a flame ionization detector (FID) and a methanizer, a 1 mL sampling loop, and a 2-m 0.32 cm diameter stainless steel column packed with Carbosphere. N_2 and [$\text{O}_2 + \text{Ar}$] were determined on a Shimadzu 8A gas chromatograph with a thermal conductivity detector. Scott Specialty gases were used as standards. Stable carbon isotopic ratios were determined using a Finnigan Mat Delta S-Gas Chromatograph Combustion Isotope Ratio Mass Spectrometer (GCC-IRMS) following methods adapted from Merrit et al. (1995). For air samples, a cryogenic focusing device was used on the front end of the gas chromatograph. The standard deviation of replicate analyses is approximately 0.15‰. The high CH_4 source gas samples were diluted to 1% CH_4 with nitrogen, and 0.1 to 0.5 mL were directly injected into the GCC-IRMS inlet system.

All 2L-canister samples were analyzed by the Blake-Rowland Laboratory at the University of California-Irvine. This laboratory has two separate high-resolution analysis systems capable of identifying and quantifying over 100 non- CH_4 hydrocarbons and halocarbons from whole gas samples using multidetector GC (gas chromatography) and combined GC-MS (mass spectrometry). The analytical apparatus utilizes three gas chromatographs (GCs) and five detectors. Each whole air sample is cryogenically trapped with liquid N_2 , warmed, and injected into a helium flow stream. This stream is then split into five, with each stream feeding a separate GC column. One DB-1, one PLOT $\text{Al}_2\text{O}_3/\text{KCl}$, one Restek-1701, and two DB-5MS columns are used. One of the DB-5MS columns is plumbed into an electron capture detector (ECD) to separate C_1 - C_2 halocarbons while the other DB-5MS is plumbed to a mass spectrometer. The Restek-1701 column is used for alkyl nitrate separation and is connected to an ECD. The DB-1/FID combination separates C_3 - C_8 hydrocarbons. The DB5MS/mass spectrometer combination quantifies C_5 - C_{10} non-methane hydrocarbons. The PLOT column, also plumbed to an FID, is used for separating C_2 - C_5 hydrocarbons, some of which are not resolved adequately by the DB-1. The preparation of standards for the halocarbons has been discussed thoroughly in previous publications (Colman et al., 2001). The range for halocarbon standards is 0.5-600 pptv, and concentration accuracies range between 1-20%. Calibration of the other NMOC compounds has been achieved by employing Scott calibration gases available in the 1-100 ppmv mixing ratio range. The measurement precisions for the halocarbons, hydrocarbons, and alkyl nitrates are in the 1-10% range.

Laboratory batch incubation studies of aerobic degradation capacity were conducted at the Danish Technical University using landfill cover soils sampled at 5-15 cm intervals, stored in darkness at 4 deg. C., sieved (8-mm), and subjected to standard physical/chemical analysis (moisture content, grain size, organic carbon, nutrients). For each incubation, 20 g. moist soil was added to a 117 ml glass serum bottle with a Mininert Teflon valve (VICI AG, Schenkon, Switzerland). Headspace air was withdrawn from each bottle using a syringe and volumetrically replaced to give an initial mixture of CH_4 (15% v/v), O_2 (35% v/v), and N_2 (50% v/v). HAP species were typically added at ranges typical of concentrations in landfill source gas (10-250 mg m^{-3}) using a gas-tight glass syringe. Samples were withdrawn according to a time series, analyzed by GC, and both mass balance and kinetic calculations were completed for various HAP species normalized to a dry mass soil basis. All tests were conducted at 22 deg. C with replicates (duplicates or greater) and appropriate abiotic controls (25 mg kg^{-1} sodium azide added). HAP compounds were quantified using a Carlo-Erba HRGC 5300 equipped with a WCOT capillary column (CP-Sil-19 CB) held isothermally at 40 deg. C, FID/ECD detectors, and nitrogen carrier gas. Calibration curves (12+-points) were constructed by adding specific volumes of pure gas components at atmospheric pressure to a known volume of air. Major gases (CH_4 , CO_2 , O_2 , and N_2) were quantified using a Chrompack Micro GC CP-2002P GC equipped with a thermal conductivity detector (TCD), a Molsieve 5A column, and a Poroplot Q column. Carrier gas was helium and column temperature was 40 deg. C. Gas standards (Microlab, Aarhus, Denmark) ranged from 0.02 to 0.5% (v/v).