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Comparative Oxidation and Net Emissions of Methane and Selected Non-Methane Organic Compounds in Landfill Cover Soils

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The surface emissions of methane (CH_4) and non-methane organic compounds (NMOCs) were determined at two different areas at a French landfill: a permanently covered and fully vegetated area (40 cm coarse sand + 80 cm of loam) and a temporarily covered area (40 cm of coarse sand). The 37 NMOCs quantified in the landfill gas samples included alkanes (C_1−C_{10}), alkenes (C_1−C_4), halogenated hydrocarbons (including (H)CFCs), and aromatic hydrocarbons. Both positive and negative CH_4 fluxes ranging from −0.01 to 0.008 g m^{-2} d^{-1} were measured from the permanently covered cell. However, high spatial variation was observed, and a hot spot with a high flux (10 g m^{-2} d^{-1}) was identified. A higher CH_4 emission occurred from the temporarily covered cell (CH_4 flux of 49.9 g m^{-2} d^{-1}) as compared to the permanently covered cell. The NMOC fluxes from the permanently covered zone were all very small with both positive and negative fluxes in the order of 10^{-7} to 10^{-5} g m^{-2} d^{-1}. Higher and mainly positive NMOC fluxes in the order of 10^{-5} to 10^{-4} g m^{-2} d^{-1} were obtained from the temporarily covered zone. The lower emission from the permanently covered and fully vegetated cell was attributable to the thicker soil layer, which functions as microbial habitat for methanotrophic bacteria. The NMOC oxidation capacity was investigated in soil microcosms incubated with CH_4. Maximal oxidation rates for the halogenated aliphatic compounds varied between 0.06 and 8.56 μg (g of soil)$^{-1}$ d^{-1}. Fully substituted hydrocarbons (tetrachloromethane, perchloroethylene, CFC-11, CFC-12, and CFC-113) were not degraded in the presence of CH_4 and O_2. Benzene and toluene were rapidly degraded, giving very high maximal oxidation rates (28 and 39 μg (g of soil)$^{-1}$ d^{-1}). On the basis of the emission measurements and the batch experiments conducted, a general pattern was observed between emissions and biodegradability of various NMOCs. The emissions mainly consisted of compounds that were not degradable or slowly degradable, while an uptake of easily degradable compounds was registered. As an example, perchloroethylene, trichloromethane, CFC-11, and CFC-12 were emitted, while atmospheric consumption of aromatic hydrocarbons and lower chlorinated hydrocarbons such as vinyl chloride, dichloromethane, and chloromethane was observed. This study demonstrates that landfill soil covers show a significant potential for CH_4 oxidation and co-oxidation of NMOCs. Under certain conditions, landfills may even function as sinks for CH_4 and selected NMOCs, like aromatic hydrocarbons and lower chlorinated compounds.

Introduction

Landfilled solid waste decomposes anaerobically with the production of CH_4 and CO_2. CH_4 from landfills is strongly implicated in global change scenarios, accounting for 5−15% of the global anthropogenic sources of CH_4 (*1*, *2*). Landfill gas (LFG) also contains trace quantities of many other hydrocarbons, including C_1−C_n species, aromatics, halogenated hydrocarbons, and organic sulfur compounds (*3*). The NMOC species are either volatilized directly from household hazardous waste materials or generated during waste degradation, where their concentrations are dependent on both original waste composition and stage of decomposition. Although the trace components make up less than 2% (v/v) of typical LFG, they may exert a disproportionate environmental burden. Emissions of carcinogens such as benzene and vinyl chloride may pose a potential threat to workers and local inhabitants (*4*). Chlorofluorocarbons contribute to the depletion of the ozone layer (*5*, *6*).

Landfill cover soils exposed to elevated concentrations of CH_4 can develop a high capacity for CH_4 oxidation by indigenous methanotrophic microorganisms; indeed, large counter-gradients for CH_4 and O_2 exist across the landfill−atmosphere interface since CH_4 concentrations in the waste are typically 50−60% (v/v) with 40−50% (v/v) CO_2 and negligible O_2. Several laboratory (*7*−*10*) and field studies (*11*−*14*) have documented high rates of CH_4 oxidation in landfill cover soils. Critical variables include soil texture and moisture content, temperature, CH_4 and O_2 concentrations, and nutrients (especially N-forms) (*15*−*18*). Cover designs engineered to optimize CH_4 oxidation have recently been developed to reduce CH_4 emissions to the atmosphere (*19*−*21*).

Methanotrophic bacteria are known to co-metabolize a variety of aliphatic compounds, including some halogenated hydrocarbons, due to the broad substrate specificity of the monooxygenase (MMO) enzyme. MMO catalyzes the oxidation of CH_4 to methanol, the first step in CH_4 oxidation (*22*). Methanotrophs in cover soils have the capacity to cometabolize selected non-methane hydrocarbons and thereby reduce emissions. Several laboratory studies have addressed the co-metabolic degradation of chlorinated hydrocarbons (especially trichloroethylene) by methanotrophs (*23*−*25*); however, most were conducted under optimal conditions with selected bacterial cultures. To date, there have been very few studies that document either oxidation rates or net

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emissions in field settings. Kjeldsen et al. (*26*) published preliminary results of laboratory studies on oxidation of CH_4 and co-oxidation of trichloroethylene (TCE) and 1,1,1-trichloroethane (1,1,1-TCA) in soil affected by LFG. High CH_4 oxidation potentials and high degradation rates for benzene and toluene were found. In addition, slow co-metabolic degradation of TCE and 1,1,1-TCA was observed in the presence of CH_4. The authors concluded that degradation processes might have a significant effect on the emission from landfill covers of the compounds studied. Bogner et al. (*27*) measured emissions of selected NMOC species at a northeastern Illinois landfill using a static chamber method. Results indicated very low emissions for the species studied (10^{-6} to 10^{-4} g m^{-2} d^{-1}) under "worst case" conditions (thin interim soil cover over recently landfilled waste). Moreover, a comparison between the sum of measured emissions at the Illinois landfill and calculated emissions using a conservative U.S. Environmental Protection Agency (EPA) regulatory model for total NMOC emissions (*28*) indicated that the EPA model overestimated emissions by more than 2 orders of magnitude.

The objective of the present study was to investigate attenuation rates and mechanisms in parallel with field measurement of net emissions at the Lapouyade Landfill in southwestern France. This study is a combined field and laboratory investigation, which provides the first complementary measurements of speciated NMOC emissions and their attenuation in landfill cover soils.

Materials and Methods

Field Location: Lapouyade Landfill. Lapouyade Landfill is located near Bordeaux in the western part of France. The site has an active gas extraction system with vertical wells and horizontal collectors. Each waste cell has a geomembrane liner coupled with engineered controls. Phase I received waste between 1996 and 1998, totaling approximately 310 000 ton of mixed waste including household waste, industrial waste, and bulky waste. Phase I cells are covered with 40 cm of coarse sand overlain by 80 cm of loam. The cover was placed in 1998 and was fully vegetated at the time of this field campaign. The Phase II area was initiated in 1998 and includes a completed zone with a temporary cover (40 cm coarse sand) and the current operational zone. The current field investigation focuses on both Phase I and the temporary cover area of Phase II.

Flux Chamber Measurements. Emission rates of CH_4, CO_2, 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 (SS) hemispheres, each with a single SS Swagelok sampling port at the top for either (i) direct sampling using syringes or (ii) 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 cm^3 over an enclosed surface area of 1217 cm^2. The volume/area ratio (cm^3 cm^{-2}) was 26.

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 necessary to achieve a 20 pptv lower limit of detection for most species, which was necessary to quantify fluxes. The sampling and analytical techniques were tested in a pilot study conducted in May 2001 at Lapouyade Landfill. In the pilot study, fluxes were compared on the basis of the extraction of two samples from a single chamber versus extraction of an initial sample from one chamber and a final sample from an adjacent chamber. In addition, trials were conducted for 60-, 120-, and 180-min sampling times. All trials yielded higher fluxes from the two samples/chamber tests versus the one sample/chamber tests, indicating that the vacuum in the canister was inducing gas flow from the soil to the chamber, elevating the observed flux. 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 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 buildup. Fluxes were calculated from the product of the change in concentration over time (dc/dt) and the [chamber volume/chamber area] ratio (*29*). Negative fluxes indicate an uptake of gases from the atmosphere by soil microorganisms, as the flux chamber concentration decreases over time. The fluxes reported herein rely on the initial value from chamber A and the final value from chamber B (adjacent).

The emission rates of CH_4 and CO_2 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 gastight syringes over 30 min and stored in preevacuated serum bottles. In general, the CH_4 concentration versus 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 CH_4 emissions (7.89 g m^{-2} d^{-1}), the final data indicate only a minor flattening of the slope with $R^2 > 0.98$. Due to the lower concentrations of trace gases as compared to CH_4 concentrations, the gas build-up effect is expected to be even less for the NMOCs assuming only diffusional fluxes.

To compare the attenuation effects, emission measurements were conducted at two different areas of the landfill. Flux chambers were installed at four locations at the final covered cell from Phase I (LP1, LP2, LP4, and LP6), which had a 0.8 m thick fully vegetated soil cover. Flux chambers were also installed at a temporary covered cell (location LP5), which had an interim cover (0.40 m) of coarse sand. Maximal emissions were expected from the thin cover in the temporary area for several reasons: minimal contact time between gases and soil, initially high outgassing of volatiles from NMOC fractions, and no time for development of methanotrophic populations due to the recent installation. The soil gas emission was also measured in a forested area outside the landfill (location LP3) to determine background emissions.

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 SS tubes (10 mm i.d.), 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. In general, samples of the main components (CH_4, CO_2, O_2, and N_2) were taken at 10-, 20-, 30-, 40-, 60-, 80-, and 100-cm depth. Samples of 25−50 mL were withdrawn with a syringe and stored in pre-evacuated serum vials. Due to the large sample volume of the vacuum (2 L), NMOC samples were taken at a maximum of four different depths (in general 30, 60, 80, and 100 cm). Samples of main components were always taken before NMOC sampling. Three soil profiles were collected from the soil on top of the finished cell (LP1, LP2, and LP6). A single profile (LP5) was collected in the temporary covered area. The soil gas probes were inserted close to the flux chambers.

Source Gas Sampling. Concentrated LFG samples were taken from the main header lines to the flare system. There were two lines: one collected gas from Phase I (four cells) while the other collected gas from two Phase I cells and nine cells from Phase II. Another sample was also taken post-

TABLE 1. Soil Parameters Describing the Final Soil Top Cover

depth (cm below surface)	soil texture	water content (% w/w)	total organic C (% org C/w)	pH
5−10	silt, sandy	3.1	1.89	6.7
15−20	silt, sandy	4.5	1.91	5.4
20−25	sand, silty	5.6	2.06	5.1
25−35	sand, silty	6.5	1.65	5.8
35−45	sand, silty	8.9	1.81	5.5
45−50	sand, silty	10.7	2.09	4.9
50−75	sand, silty	12.7	1.88	5.0
75−85	coarse sand	12.3	0.52	4.4
110−120	coarse sand	11.3	0.68	6.5

blower and pre-flare, after the lines merged; this represented the composite gas composition from the total landfill area with active gas recovery.

Soil Sampling and Analysis. Soil samples for batch studies were collected from the final covered area at location LP6, which had high CH_4 emissions, providing conditions for development of methanotrophic populations. Soil was sampled in 5-cm intervals from the surface to 30-cm depth and in 10-cm intervals from 30 to 120 cm below the surface. Soil samples were stored at 4 °C in darkness in closed plastic bags to avoid dehydration prior to the laboratory experiments. Before storage, the soil was sieved through an 8-mm mesh to increase homogeneity. The following soil analyses were carried out: soil moisture content, organic carbon content, and pH.

NMOC Gas Analysis. All 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-methane hydrocarbons (NMHCs) and halocarbons from whole gas samples using multi column/detector GC (gas chromatography) and combined GC/MS (mass spectrometry) approaches. Table 2 indicates species analyzed in this study.

The analytical apparatus utilized three GCs and five detectors. Each whole air sample was cryogenically trapped

TABLE 2. Concentrations of LFG Components and Surface Emission at Lapouyade Landfill

chamber	LFG composition (pptv)	LFG composition (μg L^{-1})	emission LP1 (g m^{-2} d^{-1})	emission LP2 (g m^{-2} d^{-1})	emission LP4 (g m^{-2} d^{-1})	emission LP6 (g m^{-2} d^{-1})	emission LP5 (g m^{-2} d^{-1})	emission LP3 (g m^{-2} d^{-1})
cover			final cover	final cover	final cover	final cover	temporary cover	forest
date			09/10/01	09/10/01	09/11/01	09/11/01	09/11/01	09/10/01
soil temp (°C)			21.6	25.3	9.7	22.2	25.0	18.9
methane	48.5% (v/v)		0.0084	−0.0095	−0.0104	10.0	49.9	−0.0033
carbon dioxide	33.7% (v/v)		8.0	13.1	15.6	77.3	107.4	19.3
Alkanes								
ethane	1 197 956	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	1 456 500	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	2 357 464	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	593 852	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	229 242	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	315 162	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	153 528	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	5 504 003	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	2 002 391	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}
isobutane	2 137 492	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}
isopentane	2 417 520	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	875 002	3.0	bdl	bdl	bdl	1.19×10^{-6}	bdl	-3.08×10^{-7}
3-methylpentane	303 290	1.0	-9.33×10^{-7}	bdl	bdl	1.78×10^{-7}	bdl	-2.33×10^{-7}
Alkenes								
ethene	4 291 703	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	3 147 014	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}
tert-2-butene	343 530	0.8	-1.94×10^{-7}	1.19×10^{-6}	bdl	bdl	2.42×10^{-5}	bdl
1-butene	153 170	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}
isobutene	1 177 236	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}
cis-2-butene	160 915	0.4	-2.67×10^{-8}	5.33×10^{-7}	bdl	-4.56×10^{-7}	1.84×10^{-5}	bdl
isoprene	155 665	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	587 526	0.6	-1.08×10^{-7}	-6.34×10^{-7}	1.34×10^{-7}	-3.50×10^{-7}	-4.65×10^{-7}	-3.89×10^{-7}
Halocarbons								
CFC-11	372 036	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	1 177 675	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	235 695	0.8	-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	462	0.0	-5.90×10^{-5}	bdl	bdl	bdl	bdl	bdl
Chlorinated Methanes								
trichloromethane	1961	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	3 033 741	10.3	-2.10×10^{-5}	2.08×10^{-7}	4.98×10^{-8}	-1.06×10^{-5}	-3.22×10^{-7}	bdl
chloromethane	28 818	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}
Chlorinated Ethylenes								
perchloroethylene	7 144 990	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	162 470	0.8	bdl	bdl	bdl	-1.08×10^{-6}	bdl	bdl
vinyl chloride	944 390	2.4	bdl	bdl	bdl	-1.03×10^{-6}	1.03×10^{-5}	bdl
Aromatics								
benzene	564 779	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	21 197 347	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	5 894 536	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)	60 272 878	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}

[a] bdl, below detection limit. CFC-11, CCl_3F; CFC-12, CCl_2F_2; HCFC-22, $CHClF_2$; H-1211, $CBrClF_2$.

TABLE 3. Maximal Methane Oxidation and Degradation Rates Obtained from Batch Experiments Containing Methane and Selected NMOCs[a]

compd studied	abbrev	initial gas concn	methane		trace components		relative
		$\mu g\ L^{-1}$	$\mu g\ g^{-1} d^{-1}$	R^2	$\mu g\ g^{-1} d^{-1}$	R^2	oxidn rate[b]
Methanes							
dichloromethane	DCM	700	28 ± 1.5	>0.996	0.885 ± 0.004	>0.996	+
trichloromethane	TCM	160	28 ± 1.5	>0.996	0.136 ± 0.004	>0.924	+
tetrachloromethane	TeCM	20	23 ± 0.8	>0.940	nd[c]		−
Ethanes							
1,1-dichloroethane	1,1-DCA	800	23 ± 0.8	>0.996	1.742 ± 0.017	>0.937	++
1,2-dichloroethane	1,2-DCA	280	29 ± 1.2	>0.987	2.809 ± 0.089	>0.931	++
Ethylenes							
vinyl chloride	VC	600	35 ± 1.1	>0.998	8.564 ± 0.385	>0.982	+++
cis-1,2-dichlorethylene	c-1,2-DCE	800	29 ± 1.2	>0.987	4.134 ± 0.048	>0.935	++
tert-1,2-dichlorethylene	t-1,2-DCE	1200	27 ± 0.1	>0.966	1.841 ± 0.013	>0.961	++
trichloroethylene	TCE	30	27 ± 0.1	>0.966	0.057 ± 0.002	>0.962	+
perchloroethylene	PCE	30	29 ± 1.2	>0.987	nd		−
Halocarbons							
Trichlorofluoromethane	CFC-11	40	34 ± 3.8	>0.980	nd		−
Dichlorodifluoromethane	CFC-12	35	34 ± 3.8	>0.980	nd		−
1,1,2-trichloro-1,2,2-trifluoroethane	CFC-113	50	34 ± 3.8	>0.980	nd		−
Dichlorofluoromethane	HCFC-21	600	18 ± 0.4	>0.981	0.189 ± 0.002	>0.983	+
Chlorodifluoromethane	HCFC-22	1000	18 ± 0.4	>0.981	0.081 ± 0.005	>0.972	+
Aromatics							
benzene	benzene	2200	31 ± 5.4	>0.989	27.9 ± 0.25	>0.983	+++
toluene	toluene	1600	31 ± 5.4	>0.989	38.7 ± 4.45	>0.987	+++

[a] Average rates and standard deviations calculated from duplicates. Regression coefficient (R^2) obtained from fitting the experimental data to a zero-order rate model. [b] Relative oxidation rates ($\mu g\ g^{-1}\ d^{-1}$): +, 0−1; ++, 1−5; and +++, >5. [c] nd, no degradation observed.

with liquid N_2, 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 $A1_2O_3$/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 C_1-C_2 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 C_3-C_8 NMHCs. The PLOT column, also plumbed to a FID, was used for separating the C_2-C_5 NMHCs, some of which were not resolved adequately by the DB-1.

The preparation of standards for the halocarbons has been discussed previously (*30*). 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. The measurement precisions for the halocarbons, hydrocarbons, and alkyl nitrates were in the 1−10% range.

Major Gases and Stable Carbon Isotopes. Major gases and stable carbon isotopes ($\delta^{13}C$) were analyzed at Florida State University, Department of Oceanography. For CH_4 and CO_2 concentrations below 1%, gas concentrations were determined on a Shimadzu 14A gas chromatograph with a flame ionization detector and a methanizer, a 1-mL sampling loop, and a 2-m 0.32-cm-diameter SS column packed with Carbosphere. N_2 and O_2 + Ar were determined on a Shimadzu 8A GC with a thermal conductivity detector. Scott Specialty gases were used as standards.

Stable 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. (*31*). For air samples, a cryogenic focusing device was used on the front end of the gas chromatograph. The cryofocusing process was conducted in two steps. In the first step, the CH_4 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 N_2 slush. After 3 min, the slush was removed, the Porapak Q column was warmed, and the CH_4 was focused onto the head of the analytical column that was held in liquid N_2. The analytical column was Poraplot Q. After an additional 3 min the analytical column was warmed, and the CH_4 passed through the Poraplot Q column into the combustion column. On the 960 °C combustion column, the CH_4 was converted to CO_2 and then entered the mass spectrometer. The standard deviation of replicate analyses is 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% CH_4 by addition with nitrogen. Samples were then analyzed by injecting 0.1−0.5 mL of sample into the GCC−IRMS inlet system (*31*).

Soil Analysis. Soil moisture content was determined gravimetrically by oven drying at 105 °C for 24 h. Soil organic matter content was determined by the loss on ignition. The pH was measured in soil−water suspensions (10 g of soil to 25 mL of 0.01 M $CaCl_2$ solution). All soil concentrations were expressed as mass of dry soil weight.

Soil Microcosms. CH_4 oxidation and degradation of trace components were examined in soil microcosms at the Technical University of Denmark. The soil was sampled near location LP6 at the final covered cell. The compounds studied included chlorinated methanes, ethanes, and ethylenes; five halocarbons; and two aromatic hydrocarbons (Table 3). A total of 20 g of soil was added to a 117-mL serum bottle capped with a butyl rubber stopper. Due to the natural dryness of the soil, a fixed amount of water (1.5 mL of Milli-Q water) was added. To obtain methane oxidation conditions, air was withdrawn from each container using a syringe and replaced with CH_4 and O_2, which gave an initial mixture of 15% CH_4, 30% O_2, and 55% N_2 (v/v). The degradation of the

trace components was determined by periodic sampling of the gas phase and analysis by GC (*10*). 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 (*10*). To check if disappearance of a compound could be due to nonmicrobial processes (abiotic degradation, sorption, and volatilization), sterilized controls were prepared by autoclaving and/or adding sodium azide (0.2 g kg^{-1}), depending on the test.

All aerobic batch experiments were conducted in duplicate at room temperature (22 °C). In general, the batch experiments were carried out with soil from the 35−40-cm depth. However, to examine oxidation rates as a function of depth, tests were also conducted with soils from various depths.

Results and Discussion

Soil Cover Design and Characteristics. The final cover for Phase I consisted of approximately 80 cm of silty to sandy loam on top of 40 cm of coarse sand. The cover was installed in 1998 and is fully vegetated with mixed grasses. The upper 35 cm of the soil was very dry with a water content below 6.5% w/w. At 50 cm below the surface, the moisture content increased and the organic carbon content showed a maximum of 2.09% w/w. The coarse sand layer had a very low organic carbon content of 0.52% w/w. The upper 35 cm of the sand layer was olive to brown in color while the underlying sand layer was dark gray, indicating very reduced conditions. Below 65 cm the smell of LFG was very strong. At 120 cm, refuse such as plastics was found. The pH of the soil water varied between 4.1 and 6.7 with minimum values at 22- and 80-cm depth. Table 1 lists the soil properties.

The temporary cover consisted of 40 cm of coarse sand/gravel. The upper 25 cm of sand was yellowish brown in contrast to the following 15 cm, which was dark and smelled strongly of LFG. The refuse appeared at 40 cm below the surface.

LFG Composition. The composite LFG in the combined headers contained 49% CH_4, 34% CO_2, 15% N_2, and 3% O_2 (v/v) (Table 2). The N_2 and O_2 indicate some air intrusion into the collection system. The $\delta^{13}C$ of the composite gas (−58.9 to −60.15‰) was identical to the $\delta^{13}C$ of gas recovered from individual wells in the temporary covered area and finished Phase I area (−59.2 to −60.3‰), indicating negligible CH_4 oxidation within the collection system (*35*).

All 37 NMOCs were detected and quantified in the LFG samples. The 37 NMOCs identified included alkanes (C_1−C_{10}), alkenes (C_1−C_4), halogenated hydrocarbons (including HCFCs), and aromatic compounds (BTEX). Of the alkanes, *n*-nonane and *n*-docane came out in relatively high concentrations (up to 28 μg L^{-1}) and together constituted approximately 60% of the total alkanes included in the analysis. In general, low concentrations of the halogenated compounds were obtained; perchloroethylene and dichloromethane were exceptions with higher concentrations of 47 and 10 μg L^{-1}, respectively. Also CFC-12 showed elevated concentrations (6 μg L^{-1}) as compared to the other fluorinated hydrocarbon compounds. The highest gas concentrations were obtained for the aromatic hydrocarbons with concentrations ranging from 25 to 86 μg L^{-1} for toluene, ethylbenzene, and xylenes. The total concentration of *m*,*p*,*o*-xylenes was 257 μg L^{-1}. Benzene was measured in much lower concentrations (<2 μg L^{-1}). In general, the NMOC concentrations in the LFG at Lapouyade Landfill tend be lower than results reported by Allen et al. (*32*) for seven co-disposal landfills in the U.K. and results compiled by Brosseau and Heitz (*33*). The data are reasonably comparable to the results of Eklund et al. (*34*) for the Fresh Kills Landfill receiving municipal solid-waste (Staten Island, NY).

LFG Emission. Emissions of CH_4 and NMOC species from final cover areas, temporary cover area, and adjacent forest area (control) are given in Table 2. The final cover area CH_4 fluxes generally varied between −0.01 and 0.008 g m^{-2} d^{-1}; only LP6 had high CH_4 flux (10.0 g m^{-2} d^{-1}). The average CH_4 flux from the surface of the finished cell was 1.97 ± 0.88 g m^{-2} d^{-1}, measured in a parallel field investigation using 23 static flux chambers randomly placed (*35*). However, high spatial variation was observed with "hot spots" exhibiting fluxes of 3.7−16.2 g m^{-2} d^{-1} (*35*). Negative CH_4 fluxes were also observed, indicating oxidation of atmospheric CH_4 and no landfill CH_4 emissions. Negative CH_4 fluxes have previously been reported in other field studies (*36*−*38*).

The temporary cell exhibited higher CH_4 emissions, averaging 37.8 ± 14.4 g m^{-2} d^{-1} (*35*) with a maximal flux of 49.9 g m^{-2} d^{-1} at LP5. In situ determination of methane oxidation is based upon measuring the difference in $\delta^{13}C$ between anoxic zone methane and methane emitted from the landfill cover soil that has been subjected to oxidation. Combined with measurement of the preference of the bacteria for $^{12}CH_4$ relative to $^{13}CH_4$, a quantitative estimate of the fraction of methane oxidized as it passes through the landfill cover soil can be determined (*11*, *12*). The average fractional CH_4 oxidation was 40 ± 7% for the cell with final cover and 3.8 ± 1.3% for the cell with temporary cover (*35*). Therefore, CH_4 oxidation was effectively lowering emissions from the final cover area, attributable to the thicker soil layer as a habitat for methanotrophic bacteria. Due to differences in climatic conditions, cover material/design, and sampling methods, a wide range of CH_4 emission rates inclusive of oxidation have been reported in the literature for landfill settings, varying between −0.0004 and 4000 g m^{-2} d^{-1} (*36*).

Table 2 gives the surface−atmosphere fluxes from the static chamber tests. In general, NMOC species measured in the composite LFG were also identified in the static chambers. The NMOC fluxes from the final cover zone were all very small with positive and negative fluxes in the order of 10^{-7} to 10^{-5} g m^{-2} d^{-1}. Species with negative fluxes included *n*-heptane, *n*-decane, ethyne, ethyl benzene, and methyl chloride. At LP6, which had high CH_4 emissions, the fluxes for aromatic hydrocarbons were negative, consistent with landfill results of Bogner et al. (*27*) and grassland results of Fukui and Doskey (*39*). NMOC flux rates from the forest station uninfluenced by LFG were lower (order of 10^{-8} to 10^{-7} g m^{-2} d^{-1}) and generally negative. Higher and mainly positive fluxes in the order of 10^{-5} to 10^{-4} g m^{-2} d^{-1} were obtained from the temporary cover area.

In the previous Illinois landfill study by Bogner et al. (*27*), emissions of most NMOC species from an area with temporary cover (45 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. In the Illinois study, the lower limit of quantification for fluxes precluded field measurement of lower fluxes from final cover areas with active gas extraction, Therefore, this is the first study to quantify fluxes from final cover areas with active gas extraction and more optimized methanotrophic activity in cover soils.

NMOCs are also emitted naturally from soil surfaces by either soil bacteria or plants. Fukui and Doskey (*39*) investigated the air−surface exchange of NMOCs at a grassland site. The average emission rates of isoprene from grassland vegetation were 4.3 × 10^{-5} g m^{-2} d^{-1}, which is higher than the isoprene fluxes measured at Lapouyade Landfill. Fukui and Doskey (*39*) found no significant air−surface exchange of alkanes, which they based on similarities of the concentrations of alkanes (propane, 2-methylpropane, *n*-butane, 2-methylbutane, *n*-pentane, *n*-hexane, 2-methylheptane, and *n*-octane) in the ambient air and the installed chambers. The average emission rates of 1-butene, 1-pentene, 1-hexene, and 1-octene were less than 2.4 × 10^{-5}

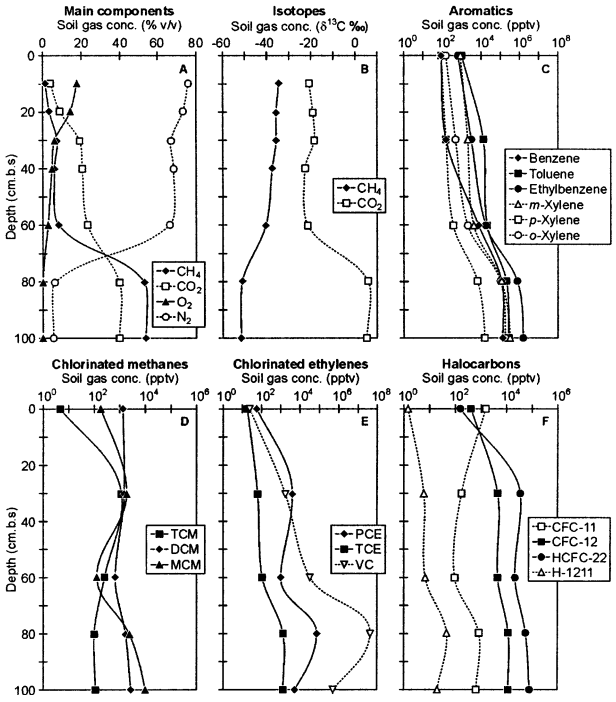

FIGURE 1. Soil gas profiles at station LP6 at the final covered cell.

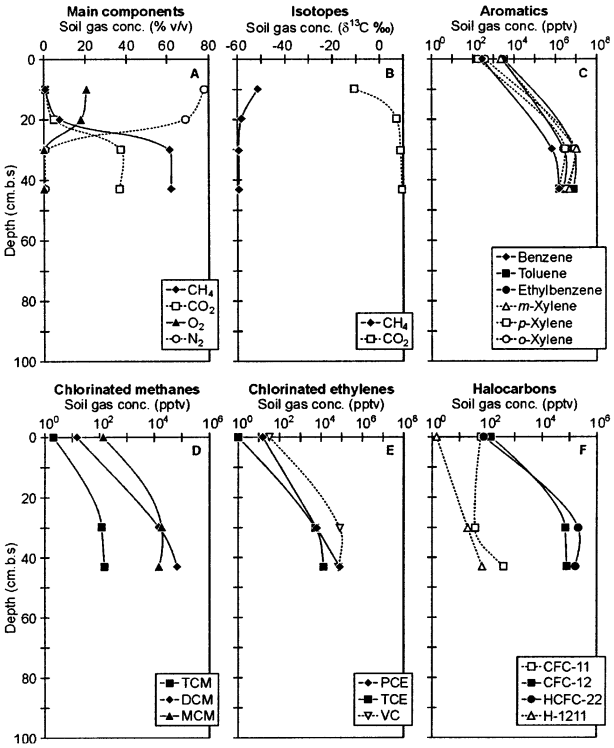

FIGURE 2. Soil gas profiles at station LP5 at the temporary covered cell.

$g\ m^{-2}\ d^{-1}$, which is comparable to the alkene fluxes from the finished waste cell at Lapouyade, but higher than the background sample, which showed uptake of most alkenes. On the basis of these results, it cannot be excluded that surface emissions of isoprene and light alkanes are from natural sources.

Soil Gas Concentration Profiles. Numerous biochemical, transport, and meteorological processes influence observed concentrations of soil gases: diffusion, advection, dilution, volatilization, sorption, biodegradation, and barometric pressure fluctuations. Although profiles are snapshots representing a single sampling episode, comparative profiles for several gases can provide information about vertical zonation of processes. In general, large differences in soil gas profiles among NMOC species, but similarities among chemically related compounds, were observed at the same location. For example, the aromatics, the alkenes, and the alkanes showed similar gas profiles within each group when plotted for the same location. This was not always the case for other groups such as the chlorinated methanes and ethylenes. Concentration profiles indicated that most NMOC species increased in concentration over several orders of magnitude from the ground surface to the top of refuse. However, some species (e.g., perchloroethylene (PCE), trichloromethane (TCM), CFC-12) had relatively constant soil gas concentrations with depth while others showed increasing gas concentrations toward the surface.

Figure 1 shows soil gas profiles for major gases and selected NMOCs at location LP6 (final cover). At 80 cm, the soil was fully anaerobic (no atmospheric N_2) with high concentrations of LFG-derived CH_4 and CO_2. The shift in CH_4 and CO_2 concentration between 60 and 80 cm indicates CH_4 oxidation. The increase in C^{13}-CH_4 together with the decrease in C^{13}-CO_2 in upward direction in the soil profile is strong evidence of CH_4 oxidation. Isotopic analysis of the emitted CH_4 using the method of Chanton (*11*, *12*) indicated that 34% of the CH_4 was oxidized at this location (*35*). The soil profiles for the majority of the NMOCs showed a decrease between 60- and 80-cm depths. Correcting the measured gas concentrations for dilution by dividing by $1 - N_{2,\text{measured}}/N_{2,\text{air}=79}$ showed that the observed decrease could only partly be explained by dilution with atmospheric air. Furthermore, the decrease in concentration was more pronounced for methyl chloride and vinyl chloride as compared to other NMOCs. The same tendency was observed at location LP1 where the concentration of vinyl chloride and HCFC-22 declined rapidly from 100 to 40 cm below the surface in comparison with PCE, CFC-11, and CFC-12, which showed very constant depth profiles (results not shown). At location LP1 the soil gas profiles for the lower chlorinated methanes showed an increase in concentration of dichloromethane (DCM) and chloromethane (MCM) toward the surface, indicating net diffusion of these compounds into the soil (results not shown).

Figure 2 shows the soil gas profiles for the main components and selected NMOCs at location LP5 in the temporary covered area. Major components indicated dominance by LFG at the 30-cm depth. At this depth, all NMOCs were present in concentrations comparable to the samples from the collection header. The shape of the concentration profiles and the overall decreasing concentrations of species from 30 cm to the surface suggest that emissions were mainly controlled by advective flow of LFG through the soil cover. At LP5, both the soil gas concentrations of NMOC species and their measured emissions were the highest observed in this study. The only exceptions were benzene and toluene, ethylbenzene, DCM, and MCM, which were being taken up by the cover. Even though the temporary cover at LP5 had been recently placed over new refuse, the soil did exhibit some methanotrophic activity as approximately 6.1% of the CH_4 was oxidized at this location based on the stable carbon isotopic method.

Methane Oxidation and Degradation of Trace Components in Soil Microcosms. Figure 3A shows the CH_4, O_2, and carbon dioxide concentrations measured in headspace versus time in a batch experiment containing HCFCs. CH_4 oxidation followed zero-order kinetics, indicating that the oxidation was not CH_4-limited. The oxidation was microbially mediated as seen from comparison with the sterilized control batch (Figure 3B). Maximum oxidation rates were calculated by applying zero-order kinetics to the data describing 90% of

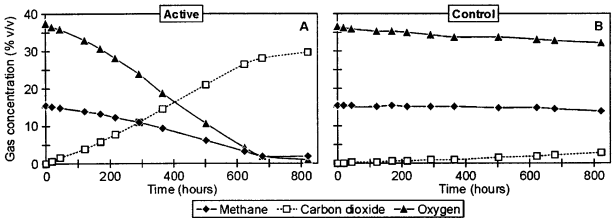

FIGURE 3. Headspace concentration of methane, oxygen, and carbon dioxide as function of time, showing methane oxidation in a batch experiment containing 20 g of soil sampled at 35−45 cm below the soil surface from the final covered cell. (A) Active batch experiment; (B) control experiment.

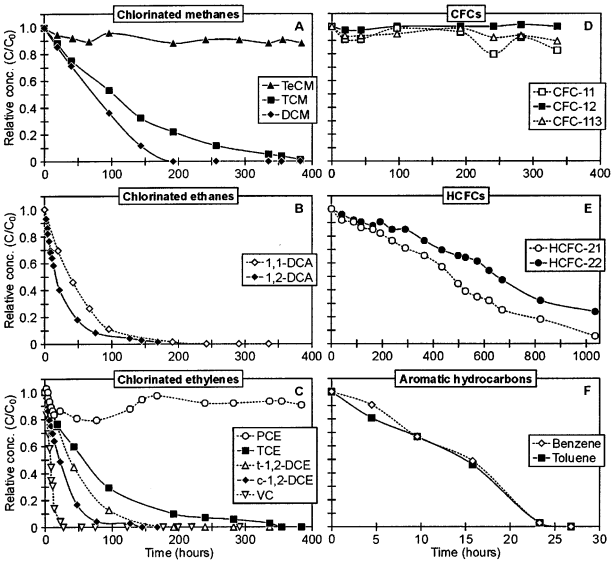

FIGURE 4. Relative headspace concentration of chlorinated hydrocarbons as a function of time in batch experiments, containing 20 g of soil sampled 35−45 cm below the soil surface from the final covered cell. (A) Chlorinated methanes; (B) chlorinated ethanes; (C) chlorinated ethylenes; (D) chlorofluorocarbons; (E) hydrochloroflourocarbons; (F) aromatic hydrocarbons. Full chemical names are given in Table 3. Please note the different time scales.

the mass transformation, which gave regression coefficients higher than 0.92 (Table 3). Lag phases were never observed, which indicates that the bacteria were well-adapted to oxidizing CH_4. The soil showed a relatively low capacity for CH_4 oxidation, resulting in oxidation rates between 18 and 35 μg of CH_4 g^{-1} d^{-1}. The CH_4 oxidation rates are very low as compared to those reported by Figueroa (*40*), who reported maximum rates between 40 and 128 μg of CH_4 g^{-1} h^{-1} for different landfill cover soils. High rates up to 112 μg of CH_4 g^{-1} h^{-1} were also obtained in batch experiments containing landfill cover soil incubated with both CH_4 and trace components conducted by Scheutz et al. (*10*). Jones and Nedwell (*41*) and Whalen et al. (*15*) obtained maximum oxidation rates between 0.65 and 2.7 μg of CH_4 g^{-1} h^{-1}, which are comparable to the results reported here. In general, very good reproducibility was obtained and results from duplicate batches were almost identical. Figure 4 shows the concentrations of trace components measured in headspace versus time in batch experiments containing 20 g of moist soil. All lower chlorinated compounds were degradable, and the degradation rates were inversely related to the chlorine/carbon ratios. For example, in batch experiments with chlorinated ethylenes, the highest rates were observed for vinyl chloride and the lowest rates were obtained for TCE, while PCE was not degraded. The degradation occurred in parallel with the oxidation of CH_4. Maximal oxidation rates for the halogenated aliphatic compounds varied between

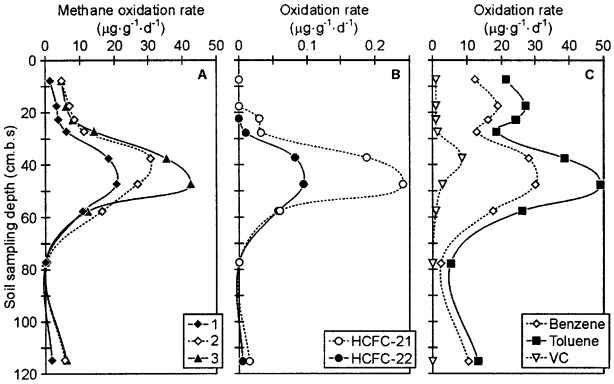

FIGURE 5. Methane oxidation and degradation rates of trace components in batch experiments as a function of soil sampling depth. (A) Methane oxidation rates in batch containing 1, HCFCs; 2, aromatics; and 3, vinyl chloride. (B) HCFCs. (C) Aromatics and VC.

0.06 and 8.56 μg g^{-1} d^{-1}. These rates are lower as compared to results obtained by Scheutz et al. (*10*), who report oxidation rates for a number of halogenated compounds in the range of 0.72 and 41 μg g^{-1} d^{-1}. Fully substituted carbons (TeCM, PCE, CFC-11, CFC-12, and CFC-113) were not degraded in the presence of CH_4 and O_2. Benzene and toluene were rapidly degraded giving relatively high maximum oxidation rates (28 and 39 μg g^{-1} d^{-1}).

Depth Distribution of Oxidation Activity. The variation of oxidation potential was determined in soil microcosms incubated with CH_4 and selected trace components, including HCFC-21, HCFC-22, vinyl chloride, benzene, and toluene. Maximal oxidation activity occurred in a zone between 40 and 50 cm below the surface, while the top 30 cm of soil showed little to no activity (Figure 5). Below 50 cm, a sharp decrease was observed with zero oxidation at 80-cm depth. The highest oxidation rates were obtained for benzene and toluene, and the depth distribution of the benzene and toluene oxidizers showed a similar pattern. However, in addition to a maximum at 50-cm depth, a smaller rate maximum was also observed at 20-cm depth, indicating a somewhat different depth distribution between the methanotrophic bacteria and the bacteria-degrading aromatics. A large number of microorganisms are known to aerobically degrade benzene and toluene; some are also able to convert chlorinated aliphatics by co-oxidation with benzene or toluene as primary substrates.

The depth containing the highest soil organic matter (50-cm depth, Table 1) corresponded to the depth that showed the highest oxidation activity (Figure 5). Since biomass is a product of biological oxidation, it is to be expected that this region should have the greatest microbial activity. A second maximum in organic matter was observed at 20 cm below surface, which is consistent with the second zone of high activity of benzene and toluene oxidizers. In controlled soil column experiments, formation of organic matter (exopolymeric substances) in CH_4 oxidation zones has been observed (*20, 42, 43*). Along with the peak in organic material, a drop in pH was observed, probably due to accumulation of acidifying oxidation products (H^+ and formic acids) as a result of increased oxidation.

Comparison of Flux Measurements, Soil Gas Profiles, and Biodegradability. *Soil Gas Profiles versus Depth Distribution of Methanotrophic Activity.* Since both CH_4 and O_2 are needed for CH_4 oxidation, the maximum oxidation zone is expected to form in a soil layer of overlapping O_2 and CH_4 gradients in stable systems (*8, 19*). CH_4 oxidation mainly occurred between 80- and 60-cm depth at the final cover (Figure 1), which is relatively deep compared to results obtained by Czepiel et al. (*7*) and Scheutz et al. (*10*), who

observed maximal oxidation at 5−20 cm in landfill soil covers. The lower oxidation zone is most likely a result of the relatively low LFG emission due to the efficient gas extraction system, which favors oxygen transport into the soil. CH_4 oxidation activity is significantly reduced when soil moisture contents decrease below 5% (*9*, *15*, *17*), and it is therefore likely that the methanotrophs in the upper part of the soil were moisture-limited rather than substrate-limited as the in situ soil moisture content was below 8% w/w. Batch incubation experiments conducted with moist soil indicated maximal oxidation capacity around 50-cm depth, which is a little higher than indicated by the gas profiles. Furthermore, it is possible that the gas profile measured that particular day is not representative for other days; it cannot be excluded that the oxidation zone moved upward.

In zones with CH_4 oxidation, a steeper decline in the degradable NMOC concentrations was observed that could only partially be attributed to dilution with atmospheric air. Furthermore, the concentrations of lower chlorinated compounds such as methyl chloride, vinyl chloride, and HCFC-22 showed a steeper decline than those of most other compounds. This was attributed to degradation since these compounds were rapidly transformed under aerobic conditions in soil microcosms (Table 3).

Fluxes versus Biodegradability. The highest oxidation capacity (33.5%) occurred around the hot spot (LP6), where the higher CH_4 flux supported methanotrophic activity. Negative flux rates were measured for dichloromethane, chloromethane, TCE, and VC at station LP6, which is in accordance with the batch experiments since these compounds displayed relatively high degradation rates. The fact that no uptake of HCFC-22 and TCM was registered at this site can be attributed to the slower degradability of these compounds. CFC-11, CFC-12, and PCE were not degradable under oxic conditions, and these compounds were all emitted at location LP6. Uptake of all aromatic hydrocarbons was registered at station LP6, which is consistent with the very high degradation rates found in the batch experiments. In the batch experiments with soil from different depths, a second maximum in oxidation rates for benzene and toluene was found for a depth of 20 cm (Figure 5), which could be a consequence of uptake from the air.

Mainly negative flux rates were measured at location LP1, which was attributed to the high effectiveness of the gas collection system. Soil gas profiles indicated that atmospheric air was drawn into the soil cover. At this location there was consistency between inward gradients, and negative flux measurements were observed.

At background station LP3, uptake of benzene, toluene, and ethylbenzene was also observed, which could be attributed to aerobic bacteria rather than to methane oxidizers since this site was not affected by LFG. Bogner et al. (*27*) also observed negative fluxes of benzene, toluene, and vinyl chloride at the Green Valley Landfill in Illinois, which in some cases was supported by soil gas profiles showing inward concentration gradients indicating diffusional uptake from the ambient air. The elevated atmospheric concentrations of NMOCs above the soil surface at the background site was due to dispersal of gas emissions from the landfill or, more likely for the aromatics, to the vehicle exhaust from the road nearby, which was used by waste trucks beginning early in the morning. The same can be said about the landfill itself where there often was a strong smell of LFG, probably from the active part of the landfill where open waste areas were positioned. Air samples downwind from the active cell had significantly greater CH_4 concentrations (17−36 ppmv) as compared with upwind samples (1.92 ppmv). Air samples collected across the landfill in the early morning before dawn had even higher CH_4 concentrations—up to 394 ppmv (*35*).

On the basis of the emission measurements and the batch experiments conducted, a general pattern was observed between emissions and biodegradability of various NMOCs. The emissions are mainly composed of compounds that are not degradable or slowly degraded, while uptake of easily degradable compounds was observed. As an example, PCE, trichloromethane, CFC-11, and CFC-12 were emitted, while atmospheric consumption was observed for the aromatic hydrocarbons and lower chlorinated hydrocarbons such as vinyl chloride, DCM, and MCM. This study demonstrates that landfill soil covers show a significant potential for CH_4 oxidation and co-oxidation of NMOCs. Under certain conditions, landfills may even function as sinks of both CH_4 and selected NMOCs including aromatic hydrocarbons and lower chlorinated compounds.

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