

Methane Fluxes from Landfills



**A Core Project of the
International Geosphere-Biosphere Programme**

GLOBAL
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Commission on Atmospheric Chemistry and
Global Pollution
of the
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Atmospheric Sciences**

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Report Edited by:

Keith A. Smith
Institute of Ecology and Resource
Management
University of Edinburgh
Edinburgh EH9 3JG
UK

Jean Bogner
Environmental Research Division (ER-203)
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439
USA

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Technical editing: Alex Pszenny

Production assistance: Elaine Robbins

Logos by Linda Kubrick

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PREFACE

The International Global Atmospheric Chemistry (IGAC) Project was initiated in the late 1980s in response to growing international concern about rapid global atmospheric chemical changes and their potential impact on humankind. IGAC is being carried out under joint sponsorship of the Commission on Atmospheric Chemistry and Global Pollution (CACGP), which is an international organization focused on the atmospheric chemical part of this system, and the International Geosphere–Biosphere Programme (IGBP), which is a broad–ranging interdisciplinary international undertaking that addresses the overall interactive Earth system including the biota.

The goals of IGAC are to develop a fundamental understanding of the processes that determine atmospheric composition, to understand the interactions between atmospheric chemical composition and physical, biospheric and climatic processes, and to predict the impact of natural and anthropogenic forcings on the chemical composition of the atmosphere. IGAC therefore addresses several urgent environmental issues including acid deposition, stratospheric ozone depletion, and climate forcing by radiatively active trace species.

IGAC both utilizes and builds on existing national programs and begins new activities. IGAC specifically provides an international framework wherein essential scientific endeavors can be accomplished, particularly when they involve large demands for scientific staff, technology, geographic coverage, or monetary resources beyond the capability of any single nation. Participation in IGAC is open to all interested scientists and is strongly encouraged. Overall scientific direction for IGAC is provided by a Scientific Steering Committee (IGAC–SSC) appointed jointly by the CACGP and the Scientific Committee for the IGBP.

The initial science plan for IGAC was developed at a CACGP Workshop held at Dookie College, Victoria, Australia, in November 1988 and was documented in a report edited by I. Galbally (CACGP, 1989). The original IGAC plan included six major scientific *Foci*, each comprised of one or more research *Activities* which address specific aspects of the IGAC goals. *Conveners* and members of *Coordinating Committees* for each Activity are appointed by the IGAC–SSC and are responsible for developing Activity research plans and coordinating their implementation.

The need was recognized early for stronger interdisciplinary approaches in developing a predictive understanding of the Earth system. The task of addressing some of the biosphere–atmosphere interaction issues was undertaken by the IGBP Coordinating Panel on Terrestrial Biosphere–Atmosphere Interactions, the SCOPE Project on Trace–Gas Exchange, and the participants of a workshop held in February 1990 in Sigtuna, Sweden. A summary of the recommendations from the CACGP and the Sigtuna workshop is included in the IGBP science plan (IGBP Report No. 12). As a result, several of the Activities described in the CACGP report were broadened to strengthen their biological aspects, several new Activities were added to the previously identified research Foci, and a new Focus on *Trace Gas Fluxes in Mid–Latitude Ecosystems* was added. This biologically oriented component was described in IGBP Report No. 13 (edited by P. Matson and D. Ojima, 1990) and is a companion to the 1989 CACGP report. In 1994, an updated description of all IGAC Activities was published as IGBP Report No. 32, entitled *IGAC: The Operational Plan* (edited by A. Pszenny and R. Prinn). Recognition of the potential for atmospheric aerosols to affect the Earth's radiative balance led to an agreement in early 1995 to merge the International Global Aerosol Program (IGAP) with

IGAC to form a new IGAC *Focus on Atmospheric Aerosols* (FAA). A booklet (edited by P. Hobbs and B. Huebert) describing this new Focus was published in 1996.

Focus 5 of IGAC addresses the topic of trace gas fluxes in temperate ecosystems in the mid-latitudes, particularly those in the Northern hemisphere which is densely populated and where the systems are subject to human disturbance through increasingly intensive agriculture, forest conversion, and acid deposition due to industrial emissions. IGAC's TRAGEX Activity seeks to document contemporary fluxes of CO₂, CH₄, N₂O and CO between the soil and the atmosphere, to determine the factors controlling these fluxes, and to improve the ability to predict future fluxes. One of the consequences of dense, and mainly urban, population in this region is the widespread disposal of refuse in landfills, the decomposition of which constitutes a significant global source of methane to the atmosphere—currently estimated to be of the same order as those from rice paddies, for example. The methods by which landfill emissions are estimated are mainly indirect and not commonly validated by direct measurement. TRAGEX therefore organized a workshop in October of 1996 that brought together experts on landfill emissions and related processes to establish the best methods for measurement and modeling and so improve the information on emissions needed as inputs to global climate models. This report summarizes the conclusions of that workshop.

Guy P. Brasseur
Chair, IGAC-SSC

May 30, 1997

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BACKGROUND AND OVERVIEW

Landfills have been identified as globally significant sources of atmospheric methane. It is expected that the landfill methane source will increase as controlled anaerobic burial of solid waste is adopted in developing countries. Published estimates for landfill methane emissions range from 9 to 70 Tg yr⁻¹ (Table 1). The most recent estimate (based on assumed rates of methane generation and emissions) suggests that landfills contribute 19 to 40 Tg yr⁻¹. Existing field measurements of methane emissions are sparse and vary over seven orders of magnitude, from 0.0004 to 4000 g m⁻² day⁻¹ (Bogner, Meadows, and Czepiel, 1997). This wide range reflects net emissions resulting from production (methanogenesis), consumption (methanotrophic oxidation), and gaseous transport processes. The various pathways into which landfill methane is partitioned are shown in Fig. 1. It can be seen from this figure that both natural and engineered controls may potentially reduce emissions.

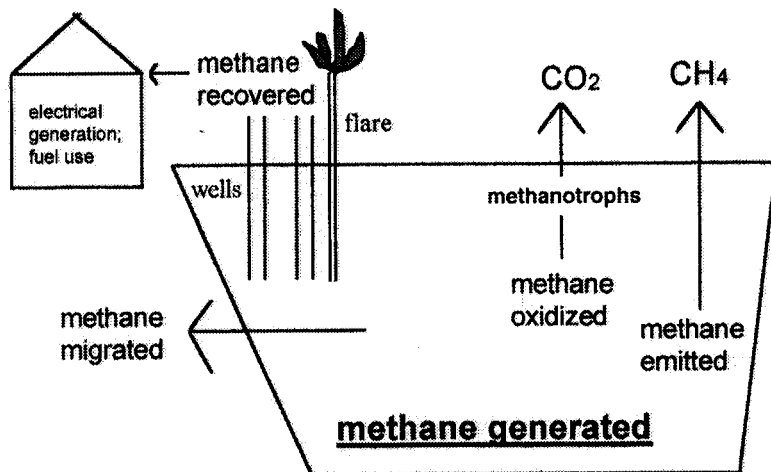
Compared to better-studied sources, there is poor understanding of how specific physical/biochemical controls affect net methane emissions from landfills. Hence, there is poor predictability regarding emission rates at sites with various cover types, climatic regimes, and management practices. In particular, methane oxidation *in situ* requires further study as a major control on net emissions. In some cases, landfill cover soils have been shown to be a sink for atmospheric methane due to high capacities for methanotrophic methane oxidation (Bogner et al., 1995; Bogner, Spokas, and Burton, 1997b). Rates of methane oxidation in landfill soils range up to 166 g m⁻² day⁻¹, among the highest for any natural setting (Whalen, Reeburgh, and Sandbeck, 1990; Kightley, Nedwell, and Cooper, 1995). Moreover, emissions of other greenhouse gases such as nitrous oxide, as well as emissions of aromatic and chlorinated compounds of environmental concern, have rarely been studied in field settings.

The purpose of this TRAGEX workshop was 1) to provide an international forum for establishing the state-of-the-art in measurement and modeling of methane emissions from landfills; and 2) to identify remaining major research issues and data needs. An overview of current work was given through invited presentations and a poster session. The presentations dealt with current global estimates (M. Barlaz); measurement methods, particularly chamber methods (J. Bogner); micrometeorological techniques (T. Meyers); methane oxidation studies (B. Svensson); and isotopic techniques for characterizing microbial methane processes (D. Coleman). The remainder of the workshop consisted of working sessions focusing on management strategies, ancillary soil studies, and modeling/scaling/inventory issues. The agenda is given in Annex A and workshop attendees in Annex B. Abstracts for the poster session are included in Annex C; these discuss preliminary results from current studies.

Table 1. Historic Global Estimates of Methane Emissions form Landfills.

<u>Estimated Emissions</u> (Tg yr ⁻¹)	<u>Source</u>	<u>Basis</u>
19-40	Doorn and Barlaz, 1995	Used current estimates for per capita refuse generation and % disposed in landfills; developed country-based estimates for urban, rural populations. Methane oxidation not considered.
33	Orlich, 1990	Used estimates for per capita refuse generation; assumed net generation (reduced to allow for methane oxidation) of either 0.086 kg methane per kg refuse (developed countries) or 0.030 kg methane per kg refuse (developing countries).
9-18	Richards, 1989	Used estimates for refuse generation proportional to GDP (gross domestic product); assumed 80% landfilled and steady-state methane generation of 0.036 kg CH ₄ per kg refuse.
30-70	Bingemer and Crutzen, 1987	Used current (mid-1980's) estimates for landfilled refuse; assumed yield of 0.1 kg methane per kg refuse with all vented to atmosphere (20% degradable organic carbon with conversion rate of 80%); steady-state methane generation from historic quantities of refuse equal to current amounts.

Landfill Methane Balance



$$\underline{\text{methane generated}} = \text{methane emitted} + \text{methane oxidized} + \text{methane recovered} + \text{methane migrated} + \Delta \text{ methane storage}$$

Figure 1. Landfill methane balance (Adapted from Bogner and Spokas, 1993).

SESSION I: FIELD MEASUREMENT STRATEGIES

Session I addressed appropriate techniques for measurement of methane and other gaseous emissions from landfill surfaces. Three tasks were established for the working group:

1. To establish the current state-of-the-art for flux measurements at different scales for methane, nitrous oxide, and nonmethane hydrocarbons.
2. To identify the most appropriate measurement technique(s) for various landfill types (differing in construction, management practices, climate, soils).
3. To establish protocols for adequate measurement of fluxes, including sampling frequency, replication, and necessary ancillary measurements.

To overcome the uncertainty associated with current estimates of regional and global landfill methane emissions, a comprehensive set of field measurements encompassing whole landfill emissions at diverse landfill types is needed. Three methods are currently

available to provide these data: enclosure, inert tracer, and micrometeorological techniques. Each of these methods has inherent advantages and disadvantages and is not uniformly applicable to the wide range of landfill configurations. The methods described below are all applicable to methane; additionally, there has been limited experience with chamber methods to measure emissions of nitrous oxide and nonmethane hydrocarbons from landfill surfaces.

Enclosure (Chamber) Methods

Enclosure methods are used to measure fluxes from individual small areas of the landfill surface (typically $<1 \text{ m}^2$). The data from a number of enclosures at a given site can be statistically analyzed to determine the whole landfill flux (Czepiel et al., 1996a). Mean estimates of this flux appear to be unbiased, regardless of the statistical distribution of the individual measurements, provided that the number of samples is adequately large. A number in excess of 100 appears to satisfy this requirement for landfill emissions. A regular gridded sampling pattern is often preferred, although small grid adjustments due to local topography may be necessary. These measurements should be performed during a period with minimal change in barometric pressure or soil moisture, preferably over 1-2 days.

Both static and dynamic methods are available for enclosure measurements. The static method is preferable for simple and low cost emission measurements over all seasons. A correlation coefficient (r) of 0.90 or higher is required for the linear regression dc/dt . Short total sampling times (less than 20-30 min.) are preferred with methane, which is typically analyzed by gas chromatography (GC/FID). Static enclosure methods are also capable of measuring net uptake of atmospheric methane by landfill soils in addition to net fluxes to the atmosphere (Fig. 2). Moreover, fluxes of nitrous oxide and nonmethane hydrocarbons (Borjesson and Svensson, 1993; Bogner, unpublished) have been measured from landfills using enclosure techniques. A disadvantage of this method is that significant time and labor investment is required to perform multiple measurements to estimate whole landfill emissions.

Tracer Methods

Tracer methods involve the release of an inert tracer gas, most commonly sulfur hexafluoride (SF_6), from the emitting surface to simulate gas emissions. The tracer gas is released from multiple points along the upwind edge of the emitting surface on a line perpendicular to the direction of the prevailing wind (Fig. 3). The number of points is dependent on the areal extent and geometry of the site. If the released tracer is well mixed in the source plume, then the methane emission rate can be obtained directly by a ratio method:

$$Q_m = Q_t (C_m/C_t)$$

where Q_m is the methane flux rate, Q_t is the tracer release rate, C_m is the measured methane concentration above background, and C_t is the measured tracer concentration.

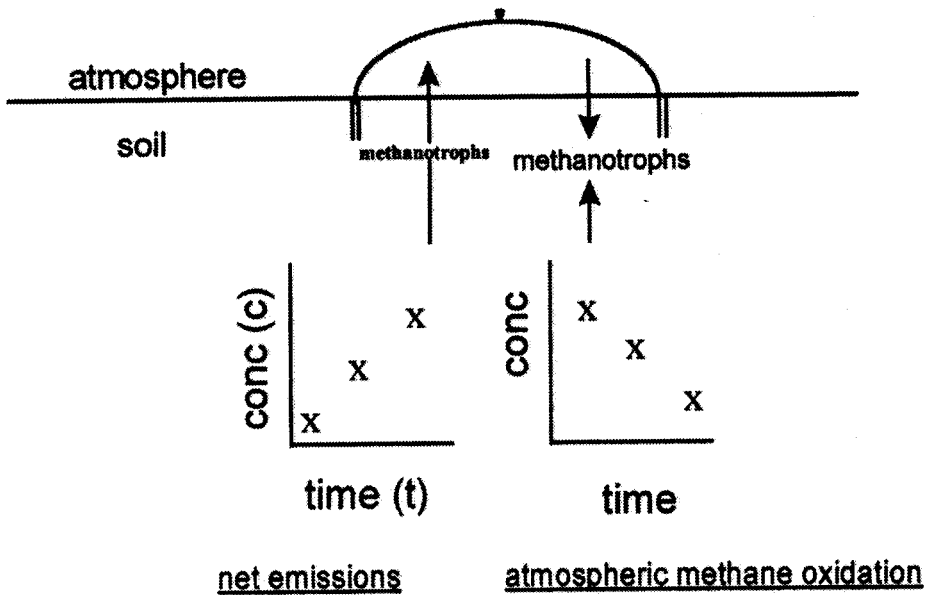
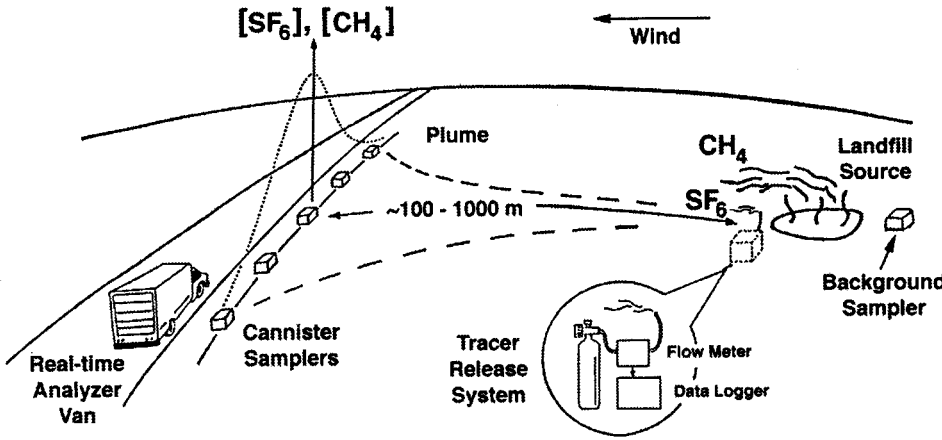


Figure 2. Use of static chambers to measure either landfill methane emissions or uptake of atmospheric methane.



$$Q_{\text{CH}_4} = Q_{\text{SF}_6} \cdot \frac{C_{\text{CH}_4}}{C_{\text{SF}_6}}$$

Figure 3. Use of tracer (SF_6) for field measurement of landfill methane emissions. (Czepiel and Mosher, unpublished).

The plume is located using a continuous analyzer for either methane or the tracer gas. It is currently cost-effective to use a continuous analyzer for the SF₆ tracer. Having identified the plume, samples are collected at ground level at several locations across the plume. These samples are analyzed for methane and SF₆ to supply the necessary ratio values above. The required distance from the landfill to downwind sampling points may be >1 km where landfills are several hundred meters on a given side (Czepiel et al., 1996a).

Atmospheric tracer methods circumvent the problem of spatial heterogeneity of the methane source by integrating the whole area flux and are therefore a favored method for emissions estimates for whole landfills. However, the potentially high cost, dependence on meteorological conditions, and potential for interfering sources of methane limits their applicability.

Micrometeorological Methods

Micrometeorological methods can also be used to evaluate whole landfill methane emissions, since they are capable of measuring fluxes across larger areas (1000's of m²) with minimal disturbance to the underlying surface. The specific footprint is determined at the time of measurement using experimental data. In addition, because these methods are more automated, they are especially useful for study of diurnal and seasonal flux variations. These methods require sophisticated instrumentation, more complex calculations, and surface constraints (relatively level terrain) which may limit their application.

Only two types of micrometeorological methods have been applied to measurement of landfill methane fluxes: eddy correlation and gradient techniques. Eddy correlation is a direct measurement of flux density determined from vertical wind velocity and concentration fluctuations, requiring concurrent measurement of the surface energy balance. This method has been used at a Tennessee landfill (USA) using a fast-response methane sensor (10 s⁻¹) based on the absorption of radiation generated with a near-infrared InGaAsP laser (Meyers et al., 1992; Hovde et al., 1995). The second method is an indirect gradient technique used in the Netherlands (Verschut, Oonk, and Mulder, 1991): flux is equal to the product of the vertical concentration gradient (obtained with conventional techniques) and a turbulent diffusivity coefficient.

Research Needs

These can be divided into three areas:

1. *Effective screening tools.* Previous investigations have shown significant spatial variability in gas flux over a given landfill. Experimental designs benefit from preliminary screening of the landfill site using a portable gas detector. This assists with the placement of a sampling grid for chambers and the location of release tubes for tracer studies. There is also a need to develop techniques which can be used in a cost-effective fashion directly to screen temporal and spatial variability in emissions. These might

include a "quick-screening" chamber technique, visual inspection of surface conditions, infrared thermography, and other approaches, all of which are best used in combination with each other and various portable gas detectors. Infrared thermography has been used in several places; however, a multiplicity of reasons for thermal anomalies (high gas flux rate, high oxidation activity, thin soil cover, localized ponding of infiltrating water in settlement depressions) must be considered.

2. *Comparison of methods for measuring gas emissions.* Landfill gas emissions have been measured by point methods and integrated area methods, but rarely by both at the same place and time. There is a need for systematic comparison of various methods under both controlled conditions and full-scale field conditions. In particular, the comparison of enclosure methods with micrometeorological and other integrated area methods is a high priority. Single point measurements by enclosure methods should be made in combination with vertical soil gas profiles. These comparisons are needed to put forward recommendations for applicability of specific techniques and to establish their limitations.

3. *Processes and governing factors.* Basic studies are needed on the variables controlling gaseous emissions. In particular, establishing the relative importance of diffusional flux to convective flux and the coupling of net flux to methane oxidation rates are important research tasks. This is likely to involve both point measurements (flux chambers, soil gas probes and laboratory incubation studies) and integrating methods (tracer techniques), which are both aided by stable isotope techniques. The importance of barometric pressure changes and rainfall (which changes the soil diffusivity/permeability) for whole-landfill emission rates must be addressed. In addition, the effect of engineered control systems (both containment and collection systems) must be quantified in field studies.

SESSION II: ANCILLARY SOIL STUDIES

Session II addressed the subject of ancillary soil studies necessary to determine controlling variables for eventual modeling and scale-up studies. Specific goals were:

1. Identification of important soil physical and biochemical variables needed to model emissions.
2. Establishment of the current state-of-the-art for measurement of methane oxidation rates, the role of methane oxidation in controlling net methane flux, and possible isotopic approaches for elucidating gross vs. net flux. Numerous investigators have recognized the importance of methanotrophic methane oxidation for regulation of landfill methane fluxes to the atmosphere (Jones and Nedwell, 1993; Nozhevnikova et al., 1993; Bogner et al., 1995; Mancinelli, 1995; Borjesson and Svensson, 1993, 1997; Boeckx, Van Cleemput, and Villalalvo, 1996; Czepiel et al., 1996b; Bogner, Spokas, and Burton, 1997b).

3. Establishment of protocols for measurement of soil physical/biochemical variables and oxidation rates.

Soil Physical and Biochemical Variables

Soil type has important effects on moisture, porosity, and tortuosity, all of which affect gaseous transport and control the availability of oxygen, methane, and nutrients to the soil microbial community. Important variables include texture, gas-filled and total porosity, dynamic water content and moisture-holding capacity, clay mineralogy, nutrient and organic matter content. The organic matter content also affects the methane-oxidizing capacity of soils. In landfill soils containing organic matter with a low C/N ratio (<13), methane oxidation can be suppressed due to increased N-turnover (Boeckx and Van Cleemput, 1996). Overall, a multidisciplinary approach is needed which combines complete characterization of different landfill soils with measurements of methane flux and methane oxidation. The latter can be studied using microbiological, isotopic, and direct measurements. Protocols should include standard methods combined with innovative approaches for multidisciplinary studies with emphasis on critical controlling variables. In the landfill setting, it is also important to recognize that soil cover design and management practices affect rates of methane oxidation and net methane emissions.

Methane Oxidation, Including Isotopic Approaches

An important control on net methane emissions is the rate of methane oxidation in cover soils; this rate is strongly affected by soil type in a given landfill setting. The physical properties of the cover soil determine available moisture, porosity, and tortuosity, all of which control the transport of oxygen, methane, and nutrients to the soil microbial community. Soil biochemical properties, particularly organic matter content and nutrients, affect the development of microbial populations.

Methane oxidation capacities for landfill cover soils are among the highest measured for any environment, in part due to historically high concentrations of methane. Methane oxidation rates are measured by laboratory or field incubation studies, often in conjunction with soil gas profile measurements and measurement of controlling variables (moisture, temperature, organic carbon content). In the case of net oxidation of atmospheric methane, static enclosure techniques yield negative fluxes which are a measure of the oxidation rate. Discussions addressed optimization of methane oxidation in cover soils through control of soil type, moisture content, and cover soil management. Previous rate studies by participants were reviewed (e.g., Fig. 4).

Isotopic approaches are attractive for quantification of methane oxidation in landfill settings. Both carbon and hydrogen isotopes can be exploited to reveal processes affecting methane oxidation and transport in landfills. The effects of oxidation on methane stable isotopes have been previously described by Coleman et al. (1981) and Barker and Fritz (1981). As methane is oxidized, the lighter isotopes are used preferentially, leaving residual methane enriched in both ^{13}C and D. The effect of this enrichment is greater for D than for C by a factor of 3 to 10 (Fig. 5). This figure shows $\delta^{13}\text{C}$ on the x axis and δD on the y axis, indicating the direction and slope of oxidation,

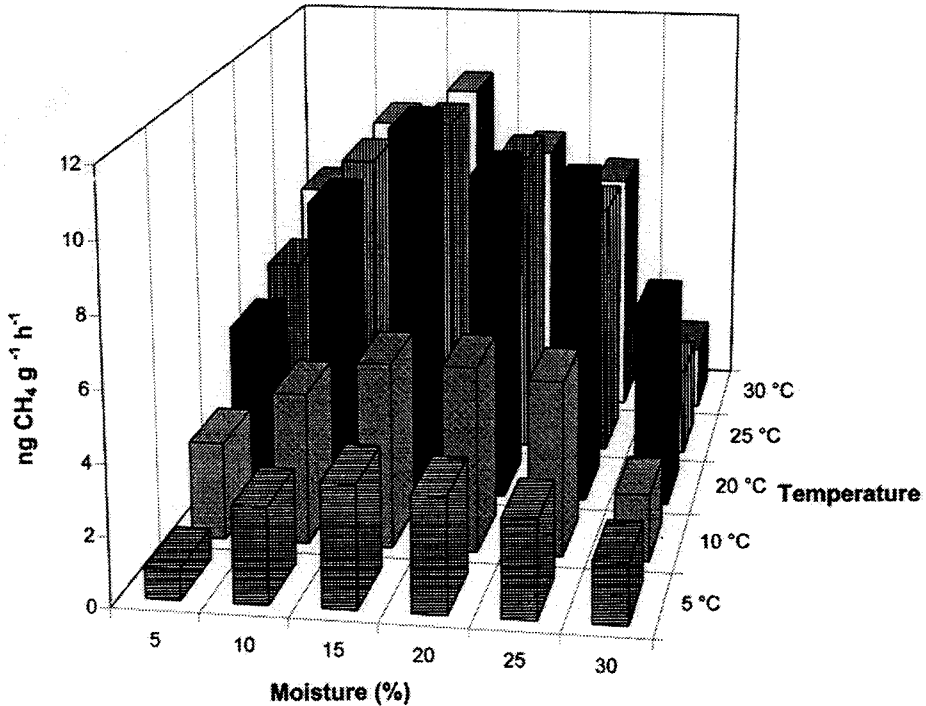


Figure 4. Methane oxidation rates as a function of soil moisture content and incubation temperature (Adapted from Boeckx, Van Cleemput, and Villaralvo, 1996)

assuming an initial $\delta^{13}\text{C}$ of -55‰ and δD of -300‰ . Several studies have shown that the $\delta^{13}\text{C}$ for landfill methane in the anaerobic zone ranges from about -50 to -60‰ while the δD ranges between about -285 to -325 (Nozhevnikova et al., 1993; Coleman et al., 1993; Bergamaschi and Harris, 1995; Bogner et al., 1996). The degree or size of the isotopic shift ($\text{D}\text{‰}$) is proportional to the fraction of methane which is oxidized and the degree of preference of the microbes for the lighter isotope (α , the fractionation factor). The fraction oxidized can be determined from the isotopic shifts ($\text{D}\text{‰}$) via Rayleigh closed system calculations (Faure, 1986) or from models of isotopic fractionation in open systems (e.g. Blair et al., 1985). These techniques have been used with success to estimate the fraction of methane oxidized in wetlands (Happell, Chanton, and Showers, 1994).

A conceptual model of methane transport through an oxidation zone is shown in Fig. 6 (Chanton, unpublished). In this model, methane may be emitted either through vents/cracks or via transport through the cover soil where oxidation may occur. One can calculate the fraction of methane oxidized during transport through the soil cap according to the open system isotopic model:

$$f_C = (\delta_B - \delta_A) / ((\alpha - 1)(1000))$$

where f_C is the fraction of methane oxidized, δ_B is the isotopic composition of methane escaping the landfill (as captured in a chamber), δ_A is the isotopic composition of methane within the anoxic zone of the landfill and α is the isotopic fractionation factor (Faure, 1986). Thus to calculate oxidation, one need only measure the isotopic composition of methane within the anaerobic zone and of the gas escaping the landfill (or within the zone of oxidation). One does not need to measure fluxes, or achieve a mass balance, although these techniques should be used in tandem to provide additional constraints on the quantification of oxidation rates. Of course, α must be known, but it can be measured in a variety of ways, for example closed system incubations where one monitors both methane concentration and isotopic composition. The isotopic fractionation effects of different trophic groups of methane-oxidizing bacteria (both H/D and $^{12}\text{C}/^{13}\text{C}$) are largely unstudied and may have significance for detailed studies of methane oxidation in landfill settings. Alternatively, it is also possible to derive values for α from depth profiles for methane, nitrogen, and ^{222}Rn in the landfill cover (Bergamaschi, 1993)

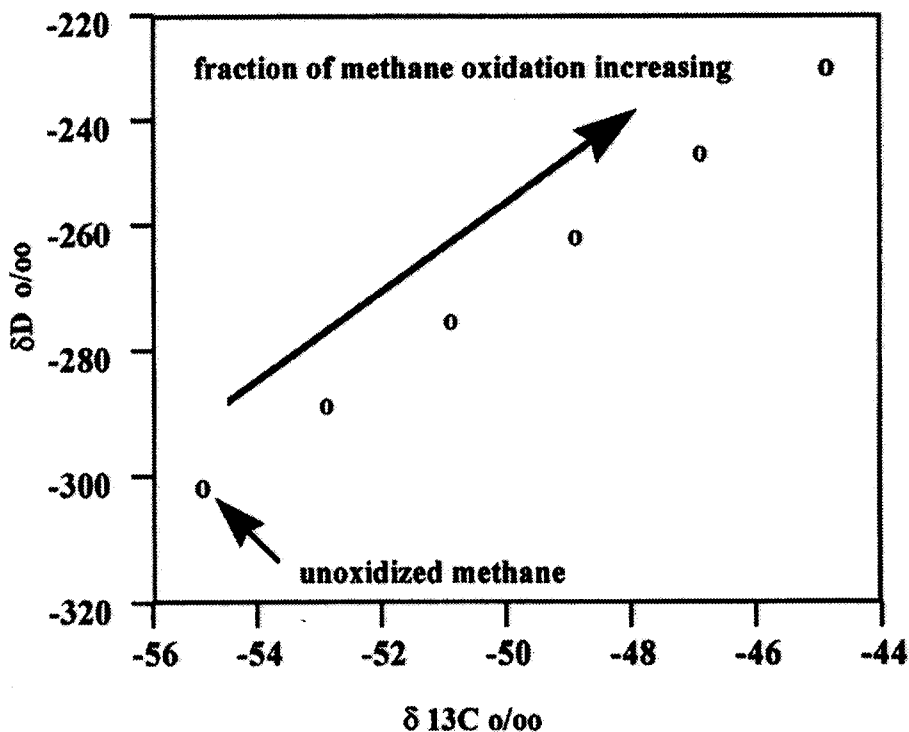


Figure 5. The differential effects of methane oxidation on $\delta^{13}\text{C}$ and δD of methane. In this example, the fractionation factor (α) for methane oxidation is 7 times larger for δD than for $\delta^{13}\text{C}$.

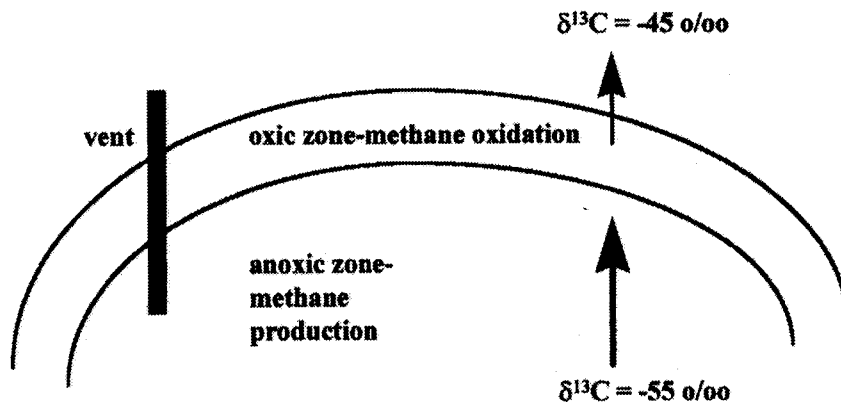


Figure 6. Use of stable isotopes to quantify methane oxidation in landfills (Chanton, unpublished). A conceptual model of a landfill is presented. Methane is produced in the anoxic zone with a $\delta^{13}\text{C}$ of -55‰ . It escapes the landfill in two ways, via vents where no oxidation occurs (this methane will have a $\delta^{13}\text{C}$ signature of -55‰), and via transport through the soil cover, where it may be oxidized by methanotrophs. In the latter case, the methane will have a $\delta^{13}\text{C}$ signature which is heavier, or ^{13}C enriched, relative to methane within the anoxic zone. The extent of this difference, D , can be related to the fraction of methane oxidized as it passes through the soil.

These isotopic techniques can be used to estimate oxidation effects at several scales. First, at the scale of chamber studies ($\sim 1 \text{ m}^2$), measurements of relative oxidation can assist with the evaluation of various oxidation enhancement techniques, including changes in soil texture, chemistry, moisture, temperature, or the status of the vegetative cover. In addition, isotopic studies might be useful in determining the relative importance of different transport pathways--e.g. transport through the soil cover vs. escape through cracks or vents (unflared). Alternatively, by sampling the downwind methane plume from a well-defined landfill source, one could quantify methane oxidation for an entire landfill system (Fig. 7). Measurements of methane oxidation on the aggregate or whole landfill level may assist with evaluating oxidation effects as a function of latitudinal variations (climate and temperature), engineered gas capture techniques, and landfill age.

Research Needs

An important issue in mitigating methane emissions from landfills is the degree of oxidation in cover soils. Therefore, a major objective of this workgroup was to establish a research agenda with regard to the effects of soil type, soil moisture, temperature, and atmospheric pressure on the methane-oxidizing capacity of cover soils and net emissions. Design and maintenance of cover soils are major controls on net emissions and require further study. A second objective was to assess how *in situ* stable

isotopic studies could be used to quantify methane oxidation. A multidisciplinary approach should be taken which combines accurate characterization of different landfill soils with measurements of methane oxidation using microbiological, stable isotopic, and direct soil measurements. Initial investigations require parallel measurement of soil physical properties with soil gas profiles in order to identify the depth of maximum methane oxidization and to assess whether oxygen, methane, or other variables might be limiting. This will also assist with determination of a minimum thickness and other properties needed for optimum oxidation. A rough calculation showed that a 20 cm layer of "bioactive" soil could potentially mitigate methane emissions from 4 m of underlying waste. The interaction of soil C and N processes, especially with respect to gaseous emissions of methane and nitrous oxide, also needs to be studied. Finally, a wide variety of soil studies in tandem with field measurements of nonmethane emissions are needed to determine whether it might be possible to use landfill cover soils as a biofilter to mitigate nonmethane emissions of environmental concern.

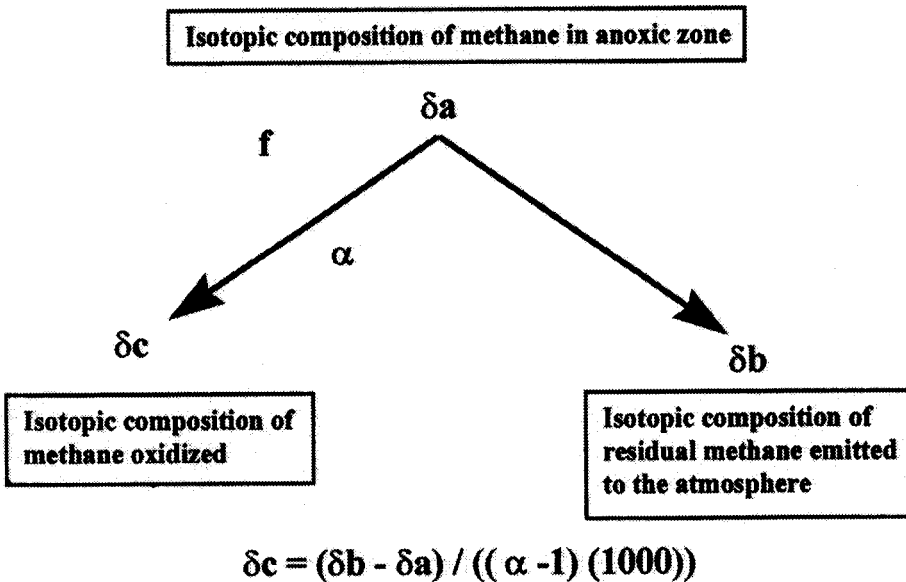


Figure 7. An open system model for isotopic fractionation as methane is transported and oxidized within landfill soils. Adapted from Blair et al., 1985.

Specific recommended studies include determination of the oxidizing capacity of different soil types incubated in various moisture, temperature, and pressure conditions. This can be done using undisturbed or reconstructed soil cores or batch incubations. These experiments are useful to indicate the effect of soil type and climatological conditions on methane oxidation, suggesting whether there might be latitudinal gradients or seasonal differences in field rates of methane oxidation. The type of organic matter (C/N ratio) can also have an important effect on the methane-oxidizing capacity of soils.

Specific isotopic studies would include both (1) *in situ* measurements in landfills under different conditions and age to gain information about local and regional methane-oxidizing capacity of cover soils; and (2) laboratory research to understand better and optimize methane oxidation in cover soils. Auxiliary isotopic investigations would include the isotopic fractionation effects of different types of methane-oxidizing bacteria and differences in the relative isotopic fractionation of H/D relative to $^{12}\text{C}/^{13}\text{C}$ in laboratory and field studies.

SESSION III: MODELING, SCALING, INVENTORY DEVELOPMENT

Session III addressed issues associated with modeling landfill methane emissions at various scales and the development of global inventories for input to climate models. Specific tasks were to:

1. Establish the state-of-the-art in modeling landfill emissions, both for global inventory estimates and at smaller scales.
2. Address the problem of scaling-up to regional and larger scales from specific site studies. Define the basis for current emission estimates, and suggest protocols for site classification and methods of scaling-up.

Current Inventories, Models

As indicated in Table 1, estimates for global landfill methane emissions have historically relied on base data consisting of statistics or estimates for refuse quantities and the fraction landfilled. The refuse generation numbers may be for portions of a given country (e.g., rural/urban), for each country as a whole, or for a group of countries with similar demographics. Three approaches are currently being used:

1. U.S. EPA (Environmental Protection Agency) approach. (Doorn and Barlaz, 1995).

This approach (Table 1) uses current estimates for per capita refuse generation and the fraction disposed in landfills in a first-order kinetic model for methane generation. Country-based estimates consider the relative number of urban to rural residents (e.g., more urban refuse is landfilled) but not methane oxidation.

2. U.K. approach (Aitchison et al., 1996).

This approach considers numerous factors shown to be important for methane emissions over time. A prime factor is the presence of a pumped gas recovery system. In general, it is a more comprehensive approach requiring more extensive data for a given country, currently focusing on U.K. statistics for landfilled refuse, the composition of the refuse in place, the presence or absence of gas collection, and methane oxidation. A time variation for generation of methane is allowed, based on a first order model (and annual data for 1970 - 1994, plus projections for 2010), as follows:

$$Q_{T,t} = k L_t e^{-k(T-t)}$$

where Q = mass of methane generated each year T by unit mass of waste landfilled in year t

L_t = specific methane generation potential of the waste

$1/k$ = decay time (to $1/e$) of the waste (default $k = 0.05 \text{ yr}^{-1}$)

Type I sites have gas recovery; type II sites do not. Gas extraction efficiency is assumed to be 70%. Biological oxidation is assumed to be 40% for type I sites, 20% for type II sites. The specific methane potential (L_t), or the total mass of methane generated by different types of waste during anaerobic decomposition, is a function of organic content and degradability. L_t is recalculated for each year in order to allow for changes in the mix of waste. Methane potential values distinguish 3 classes of waste materials: non-degradable organic (NDO), partially degradable organic (PDO), and readily degradable organic (RDO). The working assumption is that 100% of degraded carbon is eventually converted to CO_2 or CH_4 . The fraction of degraded carbon emitted as methane in landfill gas is currently estimated to be 50%, or can be generalized as:

$$r_{mc} = \text{C in CH}_4 \text{ emitted} / (\text{C in CO}_2 \text{ produced} + \text{C in CH}_4 \text{ produced})$$

Therefore, for a particular waste i , the mass of methane generated during anaerobic decay is:

$$\begin{aligned} &\text{mass of CH}_4 \text{ generated} \\ &\text{from unit mass refuse of} \\ &\text{given waste category} = r_{mc} \sum_c g_{i,c} \text{CM}_c \text{CC}_c (16/12) \end{aligned}$$

where $g_{i,c}$ is fraction of component c in waste of category I , CM_c is carbonaceous matter by weight (%), and CC_c is carbon content of carbonaceous matter by weight (%). The subscript c represents the three waste degradability components (NDO, PDO, and RDO).

3. IPCC (Intergovernmental Panel on Climate Change) approach (IPCC, 1995).

This approach is being used for country-based estimates for methane emissions from solid waste disposal sites by IPCC. The procedure is as follows: 1) estimate per capita waste production; 2) use population to estimate total waste produced; 3) estimate fraction of waste landfilled specified by country; 4) assume DOC content (%) specified by country; (5) calculate methane generation as follows:

$$(\text{MSW}_t * \text{MSW}_f * \text{MC}_f * \text{DOC} * \text{DOC}_f * F * 16/12 - R) * (1-\text{OX})$$

where:

MSW_t = total MSW generated (Gg yr⁻¹)
MSW_f = fraction MSW disposed to solid waste disposal sites
MC_f = methane correction factor (fraction)
DOC = degradable organic carbon content (fraction), which reflects composition
DOC_f = fraction DOC dissimilated
F = fraction of CH₄ in landfill gas (default is 0.5)
R = recovered CH₄ (Gg yr⁻¹)
OX = oxidation factor (fraction) (default is 0)

Certain recommendations can be made for improving this approach. In particular, the methane correction factor should be replaced by waste characterization data for a given country. In addition, algorithms which include combinations of climatic factors and landfill technology for a given country should be developed. Climatic factors include annual precipitation/evapotranspiration, mean annual temperature, and mean seasonal soil temperatures at various depths.

Recommendations and Research Needs

Improvement of models to estimate global emissions is dependent on the development of more refined methods, as well as better data for waste generation rates, waste composition, organic carbon conversion, and methane recovery. A difficult issue is the integration of results from small-scale studies to national or global emissions estimates. The current models used for global estimates have not been validated by field measurements for either net methane flux or methane oxidation rates. Recommendations for scaling-up would include the direct use of available methane flux or oxidation data where available. For many locations, national estimates could be improved through development of algorithms inclusive of specific management practices (above ground/below ground sites; gas recovery or no gas recovery), landfill size (gross size and surface to volume ratio), and realistic rates for methane oxidation. An improved methodology was developed (Fig. 8) which incorporates these factors for countries where solid waste statistics are available and field measurement programs have been completed.

WET

Landfilled Waste

DRY

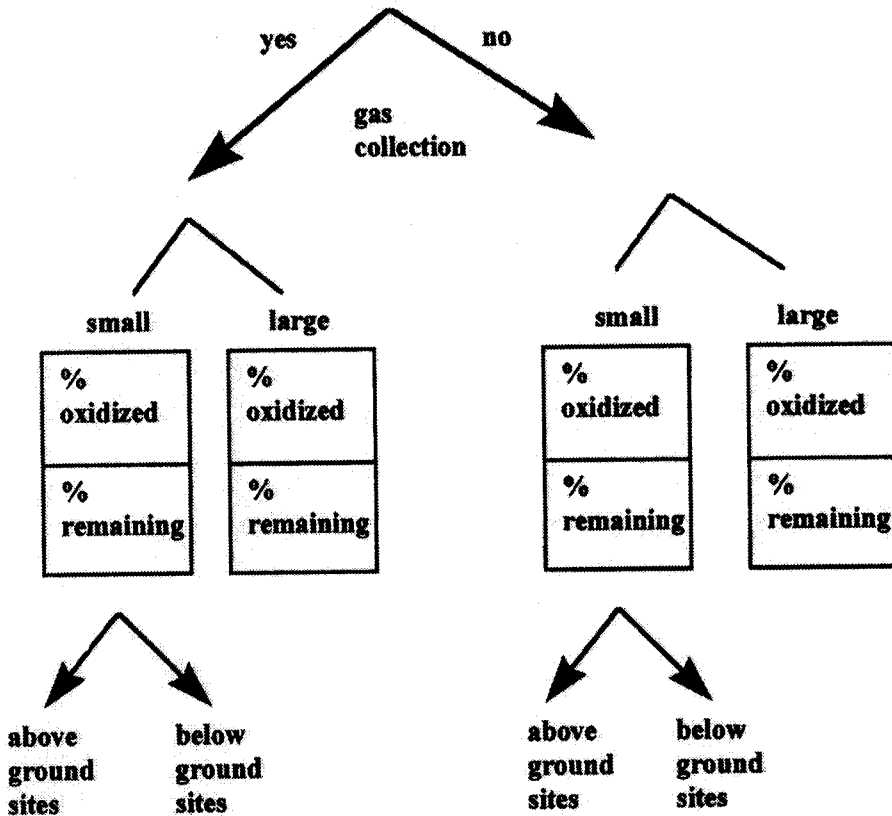


Figure 8. A conceptual model for improved quantification of country-based landfill methane emissions. This model is for developed countries with available solid waste and landfill management statistics. The primary criterion is wet vs. dry sites (based on the moisture content of the bulk landfilled waste), the second tier criterion is the presence or absence of pumped gas recovery, the third criterion is size (small vs. large), the fourth criterion is fractional methane oxidation, and the fifth criterion relates to site construction (above-ground vs. below-ground at small sites).

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ANNEX A. WORKSHOP AGENDA

DAY 1 (Mon. 21 Oct)-Arrivals and registration; welcome dinner at Freund Lodge, Argonne National Laboratory

DAY 2 (Tues 22 Oct)

08.30 Welcome from: Dr. Norman Peterson, Office of the Director, Argonne National Laboratory; Dr. Ruth Reck, Director, Climate Change Research, Argonne National Laboratory

08:40 Introduction: origins of workshop and relevance to IGAC/IGBP role in setting priorities for future research (Keith Smith/Jean Bogner)

State of the Art presentations plus discussion:

08.50 Current estimates of national and global emissions/ uncertainties
Morton Barlaz, North Carolina State University, Raleigh, North Carolina, USA

09:35 Flux measurement techniques: overview and static enclosure techniques.
Jean Bogner, Argonne National Laboratory, Argonne, Illinois, USA

10.30 Flux measurement techniques: micromet, tracer, and other integrative methods.
Tilden Meyers, National Oceanic and Atmospheric Administration, Oak Ridge, Tennessee, USA

11.05 Methane oxidation studies.
Bo Svensson, Linkoping University, Linkoping, Sweden

11:40 Isotopic studies.
Dennis Coleman, Isotech Laboratories, Inc., Champaign, Illinois, USA

12.15-12.30 General discussion

13.45-16.45 Overviews of research programs in different countries

17.00-18.30 Poster session.

DAY 3 (Wed 23 Oct)

08.30-10.30 Syndicate sessions on Research Priorities (3 parallel groups):

- 1) Flux measurements: mainly methane, but also N₂O, VOC's
- 2) Soil studies: methane oxidation; physical/chemical factors; auxiliary gas and isotopic studies
- 3) Modeling and scaling

Workshop agenda (continued)

11.00-12.30 Report back by rapporteurs

13.30-15.00 Syndicate sessions on protocols:

- 1) for flux measurement
- 2) for soil studies
- 3) for inventories: gathering of waste and landfill statistics/ site classifications

15.20-16.20 Reporting back and discussion

16:20-16.40 Introduction to final phase: producing reports

16.40- Beginning of report writing

DAY 4 (Thurs 24 Oct)

08.00-10.00 Report writing (cont.)

10.20-11.50 Presentations of draft reports

11.50-12.20 General discussion / outline of procedures for finalizing report / CLOSE

ANNEX B. PARTICIPANT LIST

Workshop Participation: **M = Measurement Methods**
 S = Ancillary Soil Studies
 I = Modeling, Scaling, Inventories
 N = None, limited attendance

Names and Addresses

John Baker [N]
WMX Technology Center
2100 Cleanwater Drive
Geneva, Illinois USA 60134
TELE 1-630-208-3221
FAX 1-630-208-9064

Morton A. Barlaz [N]
North Carolina State University
Dept. of Civil Engineering
Mann Hall/Box 7908
Raleigh, North Carolina
USA 27695-7908
TELE 1-919-515-7676
FAX 1-919-515-7908
email barlaz@unity.ncsu.edu

Pascal Boeckx [S; Rapporteur]
University of Ghent
Faculty of Agric. and Applied Biol. Sciences
Coupure 653
B-9000 Gent
Belgium
TELE 32-92-64-6002
FAX 32-92-64-6242
email Pascal.Boeckx@rug.ac.be

Jean Bogner [M,S,I]
Environ. Research Division (ER-203)
Argonne National Laboratory
9700 S. Cass Avenue
Argonne, Illinois USA 60439
TELE 1-630-252-3359
FAX 1-630-252-7415
email jean_bogner@qmgate.anl.gov

Gunnar Borjesson [M]
Swedish University of Agricultural Sciences
Dept. of Microbiology
Box 7025
S-750 07 Uppsala
Sweden
TELE 46-18-671000
FAX 46-18-673392
email Gunnar.Borjesson@mikrob.slu.se

Klaus Butterbach-Bahl [M]
Fraunhofer Inst. for Environ. Atmos.
Research
Kreuzeckbahnstrasse 19
D-82467 Garmisch-Partenkirchen
Germany
TELE 49-8821-183136
FAX 49-8821-183294
email butterbach@ifu.fhg.de

Dennis Coleman [S]
Isotech Laboratories, Inc.
1308 Parkland Court
Champaign, Illinois USA 61821-1826
TELE 1-217-398-3490
FAX 1-217-398-3493
email coleman@isotech-labs.com

Peter Czepiel [M, Rapporteur]
Harvard University
Division of Applied Sciences
Pierce Hall
20 Oxford Street
Cambridge, Massachusetts USA 02138
TELE 1-617-495-9624
FAX 1-617-495-2783
email pmc@io.harvard.edu

Arthur C. Granfield [N]
WMX Technologies, Inc.
3003 Butterfield Road
Oak Brook, Illinois USA 60521
TELE 1-630-218-1754
FAX 1-630-792-9207

Peter Kjeldsen [M, Chair]
Dept. of Environmental Engineering
Technical University of Denmark
Building 115
DK-2800 Lynby
Denmark
TEL 45-45-93-12-22 ext.1561
FAX 45-45-93-28-50
email pk@imt.dtu.dk

Jeffrey Chanton [S, Rapporteur]
Dept. of Oceanography
Florida State University
Tallahassee, Florida USA 32306
TELE 1-904-644-7493
FAX 1-904-644-2581
email jchanton@mail.fsu.edu

Martin Felker [N]
WMX Technologies, Inc
3003 Butterfield Road
Oak Brook, Illinois USA 60521
TELE 1-630-572-2962
FAX 1-630-573-2067

William J. Herz [M]
The University of Alabama
Environmental Institute
275 Mineral Industries Building
Tuscaloosa, Alabama USA 35487-0203
TELE 1-205-348-1102
FAX 1-205-348-9659
email BHERZ@coe.eng.ua.edu

Fran Kremer [S]
U.S. Environmental Protection Agency
26 West Martin Luther King Drive
Cincinnati, Ohio USA 45268
TEL 1-513-569-7346
FAX 1-513-569-7620
email kremer.fran@epamail.epa.gov

Anders Lagerkvist [I]
The Landfill Group
Lulea University of Technology
S-97187 Lulea
Sweden
TEL 46-920-91908
FAX 46-920-91468
email al@sb.luth.se

Kevin Mandernack [S]
Colorado School of Mines
Dept. of Chemistry and Geochemistry
Golden, Colorado USA 80401
TELE 1-303-384-2224
FAX 1-303-273-3629
email kmandern@mines.edu

Martin Meadows [I, Chair]
ETSU B-154
Harwell, Oxon OX11 0RA
United Kingdom
TEL 44-1235-432508
FAX 44-1235-432923
email martin.meadows@aeat.co.uk

Clayton Morlock [N]
Morlock Environmental, Inc.
1808 McIntyre Dr.
Ann Arbor, Michigan USA 48106
TELE 1-313-764-1168
email morlock@wwnet.com

Carlos Lubina [S]
Max Planck Institute for Chemistry
Dept. of Atmospheric Chemistry
Postfach 3060
D-55020 Mainz, Germany
TELE 49-6131-305-464
FAX 49-6131-305436
email lubina@mpch-mainz.mpg.de

Elaine Matthews [I, Rapporteur]
National Aeronautics and Space
Administration(NASA)
2880 Broadway
New York, New York USA 10025
TELE 1-212-678-5628
FAX 1-212-678-5552
email cxeem@giss.nasa.gov

Tilden P. Meyers [N]
National Oceanic and Atmospheric
Administration
Atmospheric Turbulence and Diffusion
Division
Oak Ridge, Tennessee USA 37831
TELE 1- 423-576-1245
FAX 1-423-576-1327
email meyers@atdd.noaa.gov

Byard Mosher [M]
University of New Hampshire
Complex Systems Research Center
Morse Hall
39 College Rd.
Durham, New Hampshire USA 03824
TELE 603-862-4520
FAX 603-862-0188
email byard@kaos.sr.unh.edu

Aldo Muntoni [M]
CISA (Environ. Sanitary Engineering Center)
via Marengo 34
09123 Cagliari
Italy
TELE 39-70-271-652
FAX 39-70-271-371

Keith Smith [M,S,I]
University of Edinburgh
Inst. of Ecology and Resource Management
West Mains Road
Edinburgh EH9 3JG
United Kingdom
TELE 44-131-535-4173
FAX 44-131-667-2601
email k.a.smith@ed.ac.uk

Bo Svensson [S, Chair]
Dept. of Water and Environmental Studies
Linköping University
S-58183 Linköping
Sweden
TELE 46-13-282280
FAX 46-13-133630
email bosseh@tema.liu.se

Alla N. Nozhevnikova [S]
Institute of Microbiology
Acad. Sci. Russia
Pr. 60 let Octiabrya 7
k.2
Moscow 117811, Russia
email allan@imbran.msk.su

A. Nozhevnikova alternative address :
EAWAG Limnological Research
Center/Biogeochemistry
Seestrasse 79
CH-6047 Kastanienbaum
Switzerland
TELE 41-41-3492153
FAX 41-41-3492168
email nozhevni@eawag.ch

Annie Tregoures [M]
Institut de Protection et de Surete
Nucleaire (IPNS)/LESI
CEA/Grenoble
17 Rue des Martyrs
38041 Grenoble Cedex 9
France
TELE 33-4-76-88-42-83
FAX 33-4-76-88-51-56
email tregoure@basilic.cea.fr

ANNEX C. ABSTRACTS

Methane Emission and Oxidation in Two Belgian Landfills

Pascal Boeckx and Oswald Van Cleemput
University of Ghent -Department of Applied Analytical and Physical Chemistry
Gent, Belgium.

It is estimated that landfills contribute 4 - 14% of the global annual methane release into the atmosphere. However, if no mitigating options are taken, landfills could become the most important single source of atmospheric methane. Two main alternatives exist to reduce methane emission from landfills. The superior option is to undertake gas recovery with associated gas use. The other option is methane oxidation in landfill cover soils. This is a cheaper and effective option especially for numerous older and smaller landfills generating low amounts of methane.

We measured the methane emission from two landfills and studied the factors controlling and regulating the methane-oxidizing capacity of their cover soils. Diffusion chambers, placed on top of the cover soil (net emission) and directly on the buried waste after removal of the cover soil (gross emission), were used. The difference between these two emission rates gives an estimate of the mitigating effect of the cover soil. From the first site an average net emission rate of $103.7 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$ was found, while from the second site the net emission varied between -5.9 (uptake of atmospheric methane) and $914.3 \text{ mg CH}_4 \text{ m}^{-2} \text{ d}^{-1}$. The gross emission was in both cases higher by a factor of $10^2 - 10^3$.

From laboratory experiments it was found that the methane oxidizing capacity of a landfill cover soil changed upon incubation conditions and time, and could be related to its nitrification rate. When a dried soil was rewetted and pre-incubated under ambient methane concentrations, the methane oxidation rate reached a maximum between day 8 and 13 ($1.40 \pm 0.12 \text{ ng CH}_4 \text{ m}^{-2} \text{ h}^{-1}$). Its methane oxidizing capacity was lost after 19 days. The nitrification rate was $5.3 \text{ mg N kg}^{-1} \text{ d}^{-1}$. When the same soil was pre-incubated under an atmosphere containing 10% (v/v) methane, oxidation rates of 7.3 and 8.1 $\text{ng CH}_4 \text{ g}^{-1} \text{ h}^{-1}$ were observed on days 8 and 19, respectively. However, under this condition the nitrification rate was reduced ($0.6 \text{ mg N kg}^{-1} \text{ d}^{-1}$). The link between nitrification and methane oxidation was also observed when methane oxidation experiments were carried out at different moisture levels and NH_4^+ -N concentrations of the soil. The reduction of the methane oxidation rate per mg NH_4^+ -N added per kg soil decreased with increasing moisture levels ($Y = 0.0018X - 0.0886$, $R^2 = 0.986$). The nitrification rate also decreased with increasing moisture levels.

From the latter two experiments it can be concluded that there is a relation between nitrification and the methane oxidation rates. This can be caused by a shift in the microbial population due to the incubation conditions. *High capacity methanotrophs* are thought to be responsible for the low nitrification rates and the high methane uptake, while *low capacity nitrifiers* are thought to be responsible for the reduced methane oxidation and the increased nitrification rates.

The moisture content of a soil strongly influences its microbial activity and the gas diffusion, and therefore controls the methane uptake rate. Third order polynomials provided the best fit for soil moisture and temperature influences. The optimum moisture level occurred at about 50% water-holding-capacity. The optimum temperature decreased with increasing moisture levels (27 - 20 °C). Using multiple-linear-regression analysis we found that the relative importance of the moisture content was higher than that of the temperature. A Q_{10} value of 1.88 ± 0.14 and an activation energy of $83.0 \pm 4.3 \text{ kJ mol}^{-1}$ were calculated.

**Greenhouse Gas Emissions at a Mid-Latitude Landfill:
Temporal Variations, Methane Oxidation, and Biogeochemical Framework**

J. Bogner and K. Spokas
Argonne National Laboratory
Argonne, Illinois USA

E. Burton
Northern Illinois University
DeKalb, Illinois USA

Using static closed chamber techniques supplemented by soil gas concentration profiles, we examined methane, nitrous oxide, and carbon dioxide (dark respiration) emissions at a mid-latitude landfill with an optimized full-scale gas recovery system. Emissions from proximal (near gas recovery well) and distal (between gas recovery wells) subsites were compared. The subsites were chosen to maximize proximal/distal differences as seen in a previous (1992-1993) transect study. Emissions of nitrous oxide and carbon dioxide were in ranges characteristic of other soil settings; however, there were no positive methane fluxes at either the proximal or distal locations during this study (July-December, 1995). Rather, the landfill surface was functioning as a sink for atmospheric methane (net methane oxidation) at rates averaging 0.007 (proximal) to 0.01 (distal) $\text{g m}^{-2} \text{d}^{-1}$. This resulted from a combination of natural and engineered control systems: lowered soil gas methane at the base of the cover soil due to the optimized gas recovery system and methanotrophic methane oxidation. Supporting field incubation studies and a whole landfill experiment (when the pumped gas recovery system was shut down and restarted) indicated that oxidation rates were able to increase rapidly over four orders of magnitude as a direct kinetic response to broad ranges of initial methane concentrations in the shallow soil and the atmosphere. Kinetic plots suggested at least two major trophic groups of methanotrophs: a methane-limited group (low methane/ambient oxygen) and an oxygen-limited group (high methane/subambient oxygen). A geochemical framework through the cover soil was developed for the three major greenhouse gases at sites with gas recovery systems:

- [surface]* I. Dominant methane oxidation zone
- II. Dominant carbon dioxide production zone.
- II/IIIa. Optimum nitrous oxide production zone.
- [top of refuse]* III. Dominant landfill gas (methane/carbon dioxide) transport zone.

**Effects of a Gas Extraction Interruption on Emissions of Methane
and Carbon dioxide From a Landfill, And on Methane Oxidation
In the Cover Soil**

Gunnar Borjesson
Swedish University of Agricultural Sciences-Department of Microbiology
Uppsala Sweden

Methane and carbon dioxide emissions from a 0.37-ha landfill containing municipal solid waste were measured using a static chamber technique and 11 permanent frames installed in a transect. Measurements were made for one week during gas extraction, a second week without gas extraction, and a third week when the system was operating again. Methane emissions ranged between -0.91 and $2930 \text{ mg CH}_4 \text{ m}^{-2} \text{ h}^{-1}$ when the extraction system was in operation, and between -0.96 and $14000 \text{ mg CH}_4 \text{ m}^{-2} \text{ h}^{-1}$ during the interruption period. The interruption resulted in enhanced methane concentrations in the cover-soil profile, especially in the surface soil (0-25 cm depth). Methane oxidation activity was significantly increased in most parts of the soil cover during the interruption, thus indicating that the activity and probably growth of methane-oxidizing bacteria increased in response to elevated methane concentrations. Based on estimates calculated from the measured emission rates, we concluded that the gas extraction system with horizontal pipelines, used at the landfill site, was capable of reducing methane emissions by approximately 90%. It was also estimated that about 50% of the methane available during the gas extraction system interruption period could become oxidized.

Contrary to methane emissions, carbon dioxide was released from 5 of the 11 chambers at higher rates during the normal extraction periods than during the interruption. This indicates that oxygen was drawn into the landfill by the extraction system, promoting increased respiration and methane oxidation processes.

Use of Stable Isotopes to Determine Methane Oxidation in Landfills

J. P. Chanton, K. Liptay, and C. Biggerstaff
Florida State University-Department of Oceanography
Tallahassee, Florida USA

P. Czepiel and B. Mosher
University of New Hampshire-Complex Systems Research Center
Durham, New Hampshire USA

W. Herz
University of Alabama-College of Engineering
Tuscaloosa, Alabama USA

Microbial oxidation of methane causes residual methane to be enriched in the heavy isotopes of carbon (^{13}C) and hydrogen (D). We suggest that as methane diffuses through soil and from a landfill, the shift in the isotopic composition of methane can yield a useful estimate of the extent and importance of methane oxidation. From measurements of methane emitted from landfills, methane from the anoxic zone of landfills, and measurements of the isotopic fractionation factor (α) associated with methane oxidation, we can calculate the fraction of methane oxidized during transit. We have approached this problem in two ways, first by using flux chambers to capture emitted methane, and second by locating and sampling the plume of the methane emanating from the landfill. The isotopic composition ($\delta^{13}\text{C}$) of methane within landfills is fairly uniform. Methane collected within the anoxic zone in landfills in New Hampshire, Alabama, and North Florida varied from -53 to -58‰, with a mean of -55 (1sd = 1.7, n = 52 measurements from 9 landfills). δD values for methane within the anoxic zone varied ranged from -307 to -295‰, with a mean of -289.8 (1sd = 7.3, n = 42 measurements from 6 landfills). Methane emanating from landfills and captured in chambers was generally ^{13}C and D enriched and ranged from -42‰ and -258‰, respectively, indicating considerable oxidation, to -56‰ and -298‰, indicating little oxidation. The percentage of methane oxidized as it diffused through the soil at 8 landfills varied from 0 to 55% with a mean of 22 (1sd = 19, n = 8). Methane collected within plumes at two landfills confirmed the difference in the relative importance of methane oxidation between the two landfills, as determined with chamber collection, but indicated a somewhat lower magnitude.

Quantification of Aggregate Methane Oxidation in a Temperate Zone Landfill Cover Soil

Peter Czepiel
Harvard University-Division of Applied Sciences
Cambridge, MA USA

Field, laboratory, and computer modeling methods were used to quantitatively assess the capability of aerobic microorganisms to oxidize landfill-derived methane (CH_4) in cover soils. The investigated municipal landfill, located in Nashua, New Hampshire, USA, was operating without gas controls of any type at the time of sample collection. Soil samples from locations of measured CH_4 flux to the atmosphere were returned to the laboratory and subjected to incubation experiments to quantify the response of oxidation to soil temperature, soil moisture, *in situ* CH_4 mixing ratio, soil depth, and oxygen content. The mathematical representations of the observed oxidation responses were combined with measured and predicted soil characteristics in a computer model to predict the rate of CH_4 oxidation in the soils at the locations of 139 measured fluxes to the atmosphere. The estimated whole landfill oxidation rate at the time of the flux measurements in October 1994 was 20%. Local air temperature and precipitation data were then used in conjunction with an existing soil climate model to estimate an annual whole landfill oxidation rate in 1994 of 10%.

Attenuation of Methane and Non Methane Organic Compounds In Landfill Gas-Affected Soils

Peter Kjeldsen, Anne Dalager and Kim Broholm
Technical University of Denmark - Department of Environ. Science and Engineering
Lyngby, Denmark

Landfill gas (LFG) contains high concentrations of methane which constitute a significant source of atmospheric methane. LFG also contains aromatic hydrocarbons (benzene, toluene) and chlorinated solvents; these can be a health threat to workers and local inhabitants and may influence the ozone layer. LFG is transported through landfill cover soil or in adjacent areas before being emitted to the air. While transported in the soil layers, the LFG is mixed with atmospheric air due mainly to diffusion processes in the soil layers (Kjeldsen, 1996). The LFG constituents may therefore be oxidized by the presence of oxygen originating from the atmospheric air. The oxidation of methane in top covers of landfills has been observed on several occasions, but trace component degradation in LFG-affected soil has not been addressed in many cases. The objective of this study was to investigate the oxidation of methane, the oxidation of the aromatic hydrocarbons benzene and toluene, and the co-oxidation of the chlorinated solvents trichloroethylene (TCE) and 1,1,1-trichloroethane (TCA) in LFG-affected soil.

The investigation was carried out in the laboratory by incubating soil samples in small closed containers with an atmosphere of methane, oxygen, and nitrogen. The containers were spiked with the organic chemicals. Control batches were made parallel to each single experiment in order to check if any disappearance could be due to non-microbial processes (abiotic degradation, volatilization and sorption). The soils were sampled at different distances from an unlined landfill where significant lateral migration of LFG is taking place. The lateral migration resulted from covering the landfill with a clay soil layer (see Kjeldsen and Fischer, 1995). Also, the emission of methane was directly studied in the field by static flux chambers. The chambers were placed at the same locations where the soils used in the laboratory experiments were sampled. In addition, soil gas probes were installed at different depths adjacent to the location of the flux chambers.

High methane oxidation rates were observed, with the highest values in soils sampled close to the landfill. The rates were higher than observed in most previous investigations of LFG-affected soils. The rates were 3-4 times higher at 25°C than at 10°C. Compared to methane emission rates observed in the flux chambers, a significant proportion of the methane emitted is potentially oxidized. Benzene and toluene were degraded in the experiments, also with the highest rates in soils sampled close to the landfill. Lag phases were observed in the soil sampled at the farthest distance from the landfill. Here the degradation first started after 1-2 days of incubation. All benzene and toluene was degraded in less than 60 hours for all incubated soils. The TCE and TCA were also degraded in the experiments when methane was present in the container. The degradation rates were, however, much lower than for benzene and toluene. By comparison of the results obtained in the laboratory with the field, it is shown that the

aerobic degradation processes in landfill soil covers and adjacent soil layers may have a significant effect on the emission of all the organic compounds studied.

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Carbon Balances at Test-Cells

A. Lagerkvist and C. Maurice
The Landfill Group
Lulea University of Technology
Lulea, Sweden

Gas emissions have been studied at twelve landfill test-cells during the period 1992-1994. These test cells are part of the integrated Swedish Landfill Gas Research Development and Demonstration (RDD) Programme. Combining the emission data with leachate, waste, and landfill gas collection data, a material balance can be derived. The leachate emission path accounted for less than 1% of both the carbon flux and the COD emission. The COD (CH_4) emissions in the gas phase were about or less than 10% of the total methane production whereas the gaseous carbon emission over the landfill surface reached a level of up to about 30% of the total carbon mobilization. The difference between carbon and COD balances can be explained by biological methane oxidation, which developed at most sampling points after 1-2 years. In some cases, even a consumption of atmospheric methane in the landfill topsoil was observed. Most of the results have been obtained during short observation campaigns in the summers, and the data need to be complemented by observations during other seasons.

Isotope Studies of Methane Oxidation in Landfill Cover Soils

C. Lubina, P. Bergamaschi, R. Königstedt, and H. Fischer
Max Planck Institute for Chemistry
Mainz, Germany

A. C. Veltkamp and O. Zwaagstra
Netherlands Energy Research Foundation
Petten, The Netherlands

The stable isotopic signatures ($\delta^{13}\text{C}$, δD) of CH_4 from German and Dutch landfill sites have been characterized by applying tunable diode laser absorption spectroscopy and isotope ratio mass spectrometry. Samples taken from the landfill gas collection systems have isotopic signatures within a small range and are typical biogenic sources dominated by acetate fermentation. In contrast to the samples from the gas collection system, soil gas samples from the landfill covers exhibit considerable variability in their $\delta^{13}\text{C}$ and δD values for CH_4 . The main reason for this behavior is the strong influence on CH_4 oxidation of methanotrophic bacteria within the landfill cover, which distinctly shifts the original $\delta^{13}\text{C}$ values (determined by methane production) towards more enriched, i.e., more positive values. This isotopic shift (maximum 19‰ V-PDB for $\delta^{13}\text{C}$ and δD) depends on the oxidation capacity of the soil. Transport parameters (soil porosity and advective transport velocity) were determined using measured N_2 mixing ratios and ^{222}Rn activities. Application of these parameters to the profile of methane mixing ratios allows calculation of the fraction of CH_4 oxidized, which is mainly controlled by the depth of penetration of atmospheric oxygen into the soil. Calculated isotope fractionation factors are in the range:

$$\alpha(\delta^{13}\text{C}) = 1.008 - 1.029 \text{ and } \alpha(\delta\text{D}) = 1.031 - 1.078$$

Chamber samples representing the small-scale fluxes into the atmosphere exhibit a very large $\delta^{13}\text{C}$ and δD (CH_4) variability, mainly due to the spatially-variable influence of methane oxidation. The shift in $\delta^{13}\text{C}$ and δD for the small-scale methane emissions is well correlated with the depth of penetration of atmospheric oxygen into the landfill cover soil. Despite the large $\delta^{13}\text{C}$ and δD variability of the single box samples, the $\delta^{13}\text{C}$ values derived from upwind-downwind measurements (representing the spatially averaged $\delta^{13}\text{C}$ of the CH_4 emissions) exhibit a very small temporal and site-to-site variability. The mean emission is significantly enriched in $\delta^{13}\text{C}$ compared to the samples from the gas collection systems. This isotopic shift can be used to calculate the amount of methane oxidized in the landfill surface before it is emitted. Assuming $\delta^{13}\text{C}$ (CH_4) fractionation factors of 1.008 - 1.029 for bacterial oxidation of methane in soil, the amount of methane oxidized in the landfill surface before it is emitted can be calculated to be 10-30% of the original methane flux.

Nitrous Oxide Emissions From Landfill Cover Soils:
A Microbiological and Stable Isotopic Investigation of N₂O Formation in Soils

Kevin Mandernack
Colorado School of Mines-Chemistry and Geochemistry
Golden, Colorado USA

Isotopic and microbiological studies of N₂O emissions from landfill cover soils indicate that some of the N₂O may be formed by nitrification via methanotrophic bacteria. Contrary to previous isotopic measurements of soil N₂O, both the $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values of N₂O collected from landfill cover soils were often enriched relative to tropospheric N₂O. The variable isotopic enrichment of N₂O reflects the degree of oxidation (nitrification) versus reduction (denitrification or N₂O reduction) within these soils. Conditions favoring reduction result in N₂O that is enriched in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$. A strong linear correlation is observed for $\delta^{18}\text{O}$ vs. $\delta^{15}\text{N}$. Average $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ values previously measured for N₂O collected from tropical soils also fall on this line. It is possible that microbial processes responsible for N₂O formation in landfill cover soils may also occur in native soils, resulting in an isotopically heavy N₂O source. This may help explain previous reports of the apparent enrichment of ^{15}N and ^{18}O in tropospheric N₂O relative to its currently known soil and oceanic sources.

Landfill Gas Recovery and Quantification of Methane Flux Reduction: Methods and Preliminary Results

Byard W. Mosher, Peter Czepiel¹, and R. C. Harriss²
University of New Hampshire-Complex Systems Research Center
Durham, New Hampshire USA

Joanne H. Shorther and Charles E. Kolb
Aerodyne Research Inc.-Center for Chemical Environmental Physics
Billerica, Massachusetts USA

Eugene Allwine and Brian K. Lamb
Washington State University-Laboratory for Atmospheric Research
Pullman, Washington USA

¹ now at Harvard University, Cambridge, Massachusetts USA

² now at NASA, Mission to Planet Earth, Washington, DC USA

Accurate field measurements are essential to constrain current uncertainties in global methane emissions from landfills, document emission reductions realized by landfill gas recovery, and test model accuracy. We have evaluated two experimental techniques (tracer flux technology and chamber flux measurements) at a 24 ha (60 acre) municipal waste landfill site in central New England, USA. Fluxes were measured prior to installation of a landfill gas recovery system using both chamber and tracer flux techniques. Chamber flux measurements ranged from the detection limit (10 mg CH₄ m⁻² d⁻¹) to 45 g CH₄ m⁻² d⁻¹. When scaled to the entire landfill surface, chamber flux measurements gave a total flux of 16.4 m³ CH₄ min⁻¹. When tracer flux methods were employed at this site, data from eight series of integrating samplers and seven mobile data sets gave a mean methane flux of 17.8 m³ CH₄ min⁻¹. The large tracer flux data set was used to examine the relationship between atmospheric pressure and methane emission. A significant inverse correlation ($r^2 = 0.84$) was observed, consistent in magnitude with that observed by other investigators. When the mean tracer flux emission value was normalized to the ambient pressure at the time of the flux chamber work, we calculated a mean flux of 16.7 m³ CH₄ min⁻¹. Thus, there appears to be very good agreement between these two experimental methods of landfill gas emissions measurement.

Recently, after installation of landfill gas recovery measures, additional tracer flux measurements were made. Although the landfill is still active, and has not been covered with a geotextile membrane, significant reductions in methane emissions of approximately 40% were measured.

Methane Production and Oxidation at Low Temperatures in Sludge Checks

A. N. Nozhevnikova and V. K. Nekrasova
Institute of Microbiology- Russian Academy of Sciences
Moscow, Russia

Municipal wastewater sludge in Russia is deposited in checks (sludge beds) to decrease moisture content before burial in landfills. Sludge deposit sites are potential sources of atmospheric methane. Methanogenesis in large landfills usually occurs under mesophilic or even thermophilic conditions. The aim of the present work was to study the methane cycle in sludge deposit sites where their internal temperature depends significantly on air temperature.

Methanogenic and methanotrophic microbial activities of samples from the Ljublinsky deposit site (Moscow) were investigated at 5-25°C. A high density of methanogenic bacteria up to 10^{10} cells cm^{-3} was characteristic of sludge beds. The rate of methanogenesis increased with the depth of sludge layer with a sharp decrease in methanogenesis in silt samples. An exponential dependence was found in the temperature interval tested. Nevertheless, stable methane production occurred at 5°C. Methanogenesis was stimulated by the addition of organic substrates and H_2/CO_2 . The most important factor for reduction of methane emissions from the sludge bed surfaces into the atmosphere was microbial oxidation of methane in the upper aerated water-and-sludge layer. Methane oxidative activity of sludge microflora was less sensitive to the lowering of temperature than methane generation. A high density of methanotrophic bacteria, averaging 10^{10} - 10^{11} cells cm^{-3} , was determined in samples from depths of 1 - 40 cm. Eleven species of methanotrophs were determined by an immunoserum method; 5 of them were able to grow at 6°C. The active psychrotrophic consortium of methanotrophic bacteria was enriched. Laboratory and field experiments have shown that the consortium of gas-oxidizing bacteria can be used for bioremediation of lands occupied by sludge deposits and landfills.

Biogas Flux Measurements from MSW Landfills Using Static and Dynamic Chambers and IR Methods

Raffaello Cossu and Aldo Muntoni

University of Cagliari-DIGITA, Department of Geoengineering and Environmental Technologies

Cagliari (Sardinia), Italy

During the summer of 1996, DIGITA (Department of Geoengineering and Environmental Technologies, University of Cagliari) started a research program on field measurements of biogas emissions from MSW landfills. Dynamic and static flux chamber were used and the results were compared to contemporaneous IR measurements. Surface emissions of CH₄, CO₂, H₂S and chlorinated compounds were measured.

Laboratory tests were carried out, and on-site test fields were set up in order to investigate the influence of a layer of MSW compost on the composition and rate of emissions.

The main results can be summarized as follows:

- Great differences in emissions were found between different points on the landfill surface; this difference was consistent even between points characterized by distances of a few meters.
- There was no significant difference between measurements carried out at different times, probably due to constant atmospheric conditions during the test period.
- Static chambers seemed to underestimate the emissions compared to dynamic chambers.
- Measurements of the emission of trace compounds was difficult using dynamic chambers; in this regard the design and the use of dynamic chambers needs to be improved.
- The use of a raw MSW compost layer as temporary cover on the landfill surface seemed to reduce emissions and improve biogas quality (removal of trace compounds):

Comprehensive Sampling and Analysis of Landfill Gas: Customized Analysis of Trace Components (CATC)

K. Spokas and J. Bogner
Argonne National Laboratory,
Argonne, Illinois USA

The complex nature of landfill gas argues for a suite of gas chromatography (GC) techniques used in combination to minimize interferences without sacrificing selectivity. We developed specialized field sampling and laboratory analytical techniques which together provide highly reproducible results for a large number of major, minor, and trace components. The CATC system (Customized Analysis of Trace Components) at Argonne National Laboratory consists of five GC's plumbed together into one laboratory analytical unit. The automated system includes three Hewlett-Packard (HP) 5890 Series II, one Varian 3700, and one SRI 8610. To date, this evolving system has been customized primarily for separation of complex landfill gas mixtures for the simultaneous analysis of major components (methane, carbon dioxide, nitrogen, oxygen, argon) and numerous trace components (hydrocarbons, aromatics, chlorinated compounds). This is accomplished by a single direct injection into the 11-column, 9-detector system (3 TCD, 4 FID, 1 ECD, 1 PID). Such a multiple column/multiple detector system provides enhanced resolution and allows for optimization of individual components while eliminating possible interferences from the remaining matrix.

Samples are taken using gas-tight syringes and stored in customized small volume (10-40 ml) pre-evacuated stainless steel sample containers. For convenient field sampling, storage, and transport of representative gas samples, the containers have been verified for storage times in excess of 3 weeks, which allows adequate time both for shipping and laboratory analysis. Such low-cost, small-volume stainless steel sample containers facilitate sampling at numerous locations on a single day and can be easily shipped from remote field sites. More importantly, use of non-trapping approaches assures the integrity of individual samples while the stainless steel construction maintains low carry-over associated with the samplers. The containers are over-pressurized in the field. When received back at Argonne, the sample container is directly connected to the GC injection system, which consists of ten sample loops plumbed into the various analytical columns/detectors. Using a vacuum pump, the sample loops are initially evacuated along with the connecting line from the loops to the container. Then the vacuum pump is isolated from the system and the sampling container valve is opened. The loops initially equilibrate at a pressure above atmospheric but are adjusted to atmospheric pressure before injection into the columns via computer-controlled sampling valves. This arrangement allows quick identification of potential container difficulties when there is insufficient pressure to fill the sampling loops. The signals from the various detectors are stored via either HP-INET linked to HP-Chemstation™ software or Peak-Simple™ software on the SRI GC unit. The system is fully calibrated via external standard methods in which known concentrations of each component are quantified with respect to detector response. This system has a repeatability of $\pm 1\%$ and an absolute accuracy of $\pm 2\%$. The Method Detection Limits (MDL) exceed 5 ppbv for the trace

components of interest. Daily calibration checks of random trace components and major gases are performed. These points are then referenced to the entire calibration library of the system since its introduction (1993). The system will automatically adjust unless a calibration point falls outside a $\pm 2\%$ window, at which time the system notifies the operator of this QA/QC failure and waits for a complete calibration check.

Measurement of Methane Emissions from Municipal Solid Waste Landfills.
Comparison of Different Methods on an Actual Landfill Site

A. Tregoures, P. Berne, M. A. Gonze, and J. C. Sabroux
Institut de Protection et de Surete Nucleaire (IPSN), France

Z. Pokryszka, and C. Tauziede
Institut National de l'Environnement Industriel et des Risques (INERIS), France

P. Cellier, and P. Laville,
Institut National de la Recherche Argonomique (INRA), France

R. Milward MIDAC Corporation Grande-Bretagne	F. Levy, and A. Anaud POLYTEC (RMP) France
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B. Burkhalter Laboratoire National d'Essais (LNE) France	D. Savanne ADEME France
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This study was funded and coordinated by *Agence de l'Environnement et de la Marise de l'Energie* (Ademe) within the framework of the French research program on the evolution of the climate and the atmosphere, with the specific aim of estimating the contribution to the greenhouse effect due to methane emitted by municipal solid waste (MSW) landfills. By comparing different methods for measuring methane fluxes on an actual landfill, the potential for practical implementation of the various methods is being evaluated. This will permit field calibration of existing emission models and, by extrapolation, will facilitate an inventory of methane emissions for all municipal solid waste landfills in France.

The present equipment and methods were first implemented in 1994 for preliminary testing at two controlled emission sites (Savanne et al., 1995). Current field experiments were conducted during July 1996 at an 8-ha MSW landfill approximately 100 km north of Paris. Accumulation chambers were developed both by INERIS and IPSN. Atmospheric methods were also implemented, including both mass balance and eddy correlation approaches developed by INRA and tracer-gas techniques developed by IPSN. Besides these ground-based methods, an airborne infrared thermography survey was carried out by the LNE to measure nighttime surface temperatures both inside the landfill (local points, ditches) and outside (roads, corn fields). The heterogeneous temperatures are likely to be related to the heterogeneous nature of emissions.

The INERIS chamber method (Pokryska et al., 1995) uses an external-recirculation chamber which is equipped with a flame ionization detector and covers an area of 0.25 m². During a one-week measurement campaign, 320 measurements were completed on the site and an additional 80 around the site. Measurements were arranged on a regular grid of approximately 20 m x 20 m. Methane fluxes varying from 0 to 3500 ml m⁻² min⁻¹ were measured, thus confirming the highly heterogeneous nature of the

emissions. [Note: All gas volumes are given at NTP.] From the field experiment results, it was possible to obtain a spatial distribution of methane flux and to compute the overall emission on the basis of multiple local measurements, using various interpolation methods. Average methane emissions were $94 \text{ ml m}^{-2} \text{ min}^{-1}$, giving a nearly $8 \text{ m}^3 \text{ min}^{-1}$ or $11500 \text{ m}^3 \text{ d}^{-1}$ total flow rate. The IPSN chamber method uses an accumulation chamber which covers an area of 0.25 m^2 and is equipped with a semiconductor SnO_2 sensor in an atmosphere dried by silicagel. A measurement campaign over 2 days resulted in 180 measurements on the site and an additional 60 in the surrounding ditches. Methane fluxes varying from 0 to $2700 \text{ ml m}^{-2} \text{ min}^{-1}$ were measured, again confirming the highly heterogeneous nature of emissions. Average emissions were calculated to be between 50 and $90 \text{ ml m}^{-2} \text{ min}^{-1}$, according to the relative weight given to the measurements in the ditches.

The eddy correlation method (INRA) systematically underestimated methane flux density, which was attributed to the spatial heterogeneity of the methane emissions. The mass balance method (INRA) relies on the principle that for a finite surface area whatever is characteristic for the flux emitted between the surface edge and the point of measurement is equal to the horizontal turbulent flux integrated over the entire height of the boundary layer. The methane flux was assessed using measurements of velocities and methane concentrations at seven altitudes (0.2, 0.4, 0.8, 1.5, 3, 6, 11 m). Wind speed was measured using anemometers. Methane concentrations were measured with an adjustable laser diode spectrometer. The measurements were confined to a limited angular sector and thus did not permit estimation of the overall emission rate. An averaged emission rate of $30 \text{ ml m}^{-2} \text{ min}^{-1}$ resulted from field measurements. The variability of emissions relative to wind direction confirmed the highly heterogeneous nature of the methane fluxes.

The tracer-gas method (IPSN) consisted of measuring the atmospheric dispersion coefficients with a tracer release combined with the use of an inversion algorithm (inverse problem) (Berne et al., 1995). Two simultaneous methods were used; all individual measurements were completed within a single day. The first method, which proved to be quite efficient, approximates the nonuniform area source as a point source to provide a total emission rate. The second method enabled us to reconstruct the source distribution with a theoretically improved accuracy. Mixing ratios were measured using gas chromatography or by open-path FTIR interferometry. These field studies provided a $70 \text{ ml m}^{-2} \text{ min}^{-1}$ averaged emission rate, which corresponds to a daily rate of 8000 m^3 for the 80000 m^2 area investigated.

Following this series of on-site experiments, we concluded that both accumulation chamber and tracer-gas methods can give an estimation of the right order of magnitude for the total emission rate. The mass-balance method investigated only a limited sector of the landfill. However, chamber methods enabled us to assess the pronounced spatial variability of the emission rates. On the other hand, atmospheric methods, which directly yield the flow-rate of methane, are more dependent on the meteorological conditions. In all likelihood, no single method will be sufficient to address the problem of measuring the methane flow rate from a given landfill. The choice of a measurement method should take into account both the technical (required precision,

continuous or point measurements) and economic aspects (duration and cost of the measurements) of an actual methane survey.

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Savanne, D., P. Cassini, Z. Pokryszka, C. Tauziède, A. Tregoures, P. Berne, J.C. Sabroux, P. Cellier, and P. Laville, 1995, *A comparison of methods for estimating methane emissions from MSW landfills*, Proc. Sardinia '95 Fifth International Landfill Symposium, CISA, Univ. of Cagliari, Sardinia.

ANNEX D: CURRENT IGAC FOCI, ACTIVITIES, AND ACTIVITY CONVENERS

- | | |
|---------------------------|---|
| <i>Marine Focus</i> | <ul style="list-style-type: none"> •North Atlantic Regional Experiment (NARE), F.C. Fehsenfeld, USA & S.A. Penkett, UK •Marine Aerosol and Gas Exchange (MAGE), B.J. Huebert, USA •East Asian/North Pacific Regional Experiment (APARE), H. Akimoto, Japan |
| <i>Tropical Focus</i> | <ul style="list-style-type: none"> •Biosphere–Atmosphere Trace Gas Exchange in the Tropics: Influence of Land Use Change (BATGE), R.A. Delmas, France & M. Keller, USA •Deposition of Biogeochemically Important Trace Species (DEBITS), J.–P. Lacaux, France •Biomass Burning Experiment: Impact on the Biosphere and Atmosphere (BIBEX), M.O. Andreae, Germany •Rice Cultivation and Trace Gas Exchange (RICE), H.–U. Neue, Germany & R.L. Sass, USA |
| <i>Polar Focus</i> | <ul style="list-style-type: none"> •Polar Atmospheric and Snow Chemistry (PASC), L.A. Barrie, Canada & R.J. Delmas, France |
| <i>Boreal Focus</i> | <ul style="list-style-type: none"> •High Latitude Ecosystems as Sources and Sinks of Trace Gases (HESS), W.S. Reebergh, USA |
| <i>Mid–Latitude Focus</i> | <ul style="list-style-type: none"> •Trace Gas Exchange: Mid–Latitude Ecosystems and Atmosphere (TRAGEX), G.P. Robertson, USA & K.A. Smith, UK |
| <i>Global Focus</i> | <ul style="list-style-type: none"> •Global Tropospheric Ozone Network (GLONET), J.M. Miller, Switzerland & V.A. Mohnen, USA •Global Atmospheric Chemistry Survey (GLOCHEM), E.L. Atlas, USA •Global Tropospheric Carbon Dioxide Network (GLOCARB), P. Ciais, France & N.B.A. Trivett, Canada •Global Emissions Inventory Activity (GEIA), <i>To be named</i> •Global Integration and Modeling (GIM), P.S. Kasibhatla, USA & M. Kanakidou, France |
| <i>Fundamental Focus</i> | <ul style="list-style-type: none"> •Nitrous Oxide and Halocarbons Intercalibration Experiment (NOHALICE), P.J. Fraser, Australia •Non–Methane Hydrocarbon Intercomparison Experiment (NOMHICE), J.G. Calvert & F.C. Fehsenfeld, USA •Carbon Dioxide Intercalibration Experiment (CARBICE), P. Ciais, France & N.B.A. Trivett, Canada •Atmospheric Chemistry and Environmental Education in Global Change (ACE^{ED}), K.L. Demerjian, USA |
| <i>Aerosol Focus</i> | <ul style="list-style-type: none"> •Aerosol Characterization and Process Studies (ACAPS), T.S. Bates, USA & J.L. Gras, Australia •Direct Aerosol Radiative Forcing (DARF), T. Nakajima, Japan & J.A. Ogren, USA •Aerosol–Cloud Interactions (ACI), T. Choulaton, UK, & D.A. Hegg, USA •Stratospheric and Upper Tropospheric Aerosols (SUTA), A. Ansmann, Germany and M.P. McCormick, USA |

ANNEX E: IGAC SCIENTIFIC STEERING COMMITTEE (1997) AND OFFICES

SSC
Chair: Guy P. Brasseur
Atmospheric Chemistry Division
National Center for Atmospheric Research
P.O. Box 3000, Boulder, CO, 80307-3000, USA
Tel: (+1-303) 497-1456; Fax: (+1-303) 497-1415
E-mail: brasseur@ncar.ucar.edu

SSC
Members: Paulo Artaxo (Brazil)
Jariya Boonjawat (Thailand)
Ralf Conrad (Germany)
Robert J. Delmas (France)
Jost Heintzenberg (Germany)
Peter V. Hobbs (USA)
Barry J. Huebert (USA)
Vyacheslav Khattatov (Russia)
Yutaka Kondo (Japan)
Shyam Lal (India)
Patricia A. Matrai (USA)
John M. Miller (Switzerland)
Heinz-Ulrich Neue (Germany)
Stuart A. Penkett (UK)
Mary C. Scholes (South Africa)
Sjaak Slanina (Netherlands)
Neil B.A. Trivett (Canada)
Wang Mingxing (China)

IGAC Core Project Office
Building 24-409
Massachusetts Institute of Technology
Cambridge, MA 02139-4307, USA
Tel: (+1-617) 253-9887
Fax: (+1-617) 253-9886
E-mail: pszenny@mit.edu

European IGAC Project Office
Environment Institute
CEC Joint Research Centre
I-21020 Ispra (Varese), Italy
Tel: (+39) 332 78 95 67
Fax: (+39) 332 78 50 22
E-mail: stanislaw.cieslik@jrc.it

South Asian IGAC Project Office
National Physical Laboratory
Dr. K.S. Krishnan Road
New Delhi 110012, India
Tel: (+91-11) 578-7162
Fax: (+91-11) 575-2678
E-mail: npl@sirnetd.ernet.in