

# Temporal Variations in Greenhouse Gas Emissions at a Midlatitude Landfill

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## ABSTRACT

A field study encompassing a parallel time series of CH<sub>4</sub>, N<sub>2</sub>O, and CO<sub>2</sub> emissions measurements was completed by using static enclosure techniques at a midlatitude landfill (northeastern Illinois) during the period of July through December 1995. The site had a pumped gas recovery system and thus a high level of engineered gas control. No net CH<sub>4</sub> emissions to the atmosphere were measured during this study; rather, the landfill cover soils were functioning as a sink for atmospheric CH<sub>4</sub>. The net measured emissions of CO<sub>2</sub> (dark respiration) and N<sub>2</sub>O were in ranges characteristic of natural soils and were dependent on similar controls, including temperature, moisture, and aeration status. A comparison of proximal (near gas recovery well) and distal (between wells) emissions with soil gas profiles permitted development of a conceptual biogeochemical model for gas transport and reaction through the landfill cover. This model includes a modified reduction sequence where the major zones (from ground surface downward) were a near-surface zone of optimum CH<sub>4</sub> oxidation; a zone of optimum CO<sub>2</sub> production (predominantly from root zone respiration); a zone of optimum N<sub>2</sub>O production; and a deep zone dominated by transport of landfill gas (CH<sub>4</sub> and CO<sub>2</sub>) from methanogenic production zones in the underlying refuse.

AS SITES of controlled anaerobic burial of approximately 60% of U.S. municipal solid waste (USEPA, 1994), sanitary landfills are implicated as the largest anthropogenic source of atmospheric CH<sub>4</sub> in the USA (USEPA, 1993). For national and global inventories of greenhouse gases, landfill CH<sub>4</sub> emissions have been estimated with a "top-down" approach that uses estimated CH<sub>4</sub> generation from an assumed mass of buried refuse as a surrogate for emissions. The resulting worldwide landfill emissions estimates have ranged widely, from 9 to 70 Tg CH<sub>4</sub> yr<sup>-1</sup> (Bingemer and Crutzen, 1987; Richards, 1989) to a total annual atmospheric burden from all sources of 535 Tg ( $\pm$  125) CH<sub>4</sub> (IPCC, 1995).

Relatively few field measurements of CH<sub>4</sub> and other major greenhouse gas emissions have been made at landfills, and temporal variability has been largely unaddressed in quantitative field studies. The sparse literature on actual field measurements of landfill CH<sub>4</sub> emissions indicates wide ranges, from negative emissions (net oxidation of atmospheric methane by indigenous methanotrophs) to positive emissions spanning roughly seven orders of magnitude (from <0.0004–4000 g m<sup>-2</sup> d<sup>-1</sup>) (Bogner et al., 1997b, and references cited therein). Studies in Sweden have reported CO<sub>2</sub> and N<sub>2</sub>O emis-

sions from landfill sources and seasonal variations in CH<sub>4</sub> oxidation (Borjesson and Svensson, 1993; 1997a, b). However, parallel emissions and profiles of the three major greenhouse gases (CH<sub>4</sub>, N<sub>2</sub>O, and CO<sub>2</sub>) have not been previously reported. Typically, the final landfill cover consists of 1 to 2 m of compacted clay overlaid by recycled "topsoil" that has been seeded to promote vegetative growth and the development of a functional soil microbial ecology. Recently, in the USA, final cover designs including a geomembrane (high density polyethylene layer) have been implemented in response to landfill regulations under Subtitle D of the Resource Conservation and Recovery Act. On a surface area basis, however, the vast majority of existing municipal solid waste landfills in the USA and worldwide do not include a geomembrane composite cover.

After landfill burial, anaerobic conditions are rapidly established in the refuse. The breakdown of complex carbohydrates, proteins, and other degradable organic materials occurs via a series of microbial reactions through intermediate carboxylic acids to CH<sub>4</sub> and CO<sub>2</sub> in roughly equimolar proportions. Methanogenesis occurs via biogenic pathways of acetate cleavage or CO<sub>2</sub> reduction. Carbon dioxide is internally produced and recycled by several mechanisms, including direct oxidation of organic C (aerobic), anaerobic fermentative reactions, methanogenesis by acetate cleavage, transport in an aqueous phase, and aerobic methanotrophic methane oxidation. In profile, a landfill is characterized by short vertical distances between the highly anaerobic zone of methanogenesis in the refuse and increasingly more aerobic soils toward the top. The aerobic cover soils have the highest reported capacities of any soils for methanotrophic methane oxidation (Whalen et al., 1990; Knightley et al., 1995; Mancinelli, 1995; Bogner et al., 1995a, 1997a; Borjesson and Svensson, 1997c; Boeckx and Van Cleemput, 1996; Boeckx et al., 1996; Czepiel et al., 1996). Competing soil microbiological processes over short vertical distances combined with distinct physical boundaries at interfaces can result in steep gradients and slope reversals in the concentration profiles of soil gases. The net emissions of a given gas are thus a function of the dynamics of production, transport, and consumption processes. As in natural soils, most of the pertinent processes for C and N cycling are microbially driven; thus, they depend on moisture, temperature, available nutrients, substrate quality, competing trophic groups, and other factors.

Two major shortcomings arise with respect to gaseous C and N cycling processes at landfills in the context of global greenhouse gas budgets. One is that studies to date have emphasized CH<sub>4</sub> emissions alone; thus, coupled rates for N<sub>2</sub>O and CO<sub>2</sub> remain undetermined. The

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second is that the typical time frame of previous investigations has been limited to short-term (snapshot) measurements of CH<sub>4</sub> emissions. The objectives of the current study were to develop a time sequence of parallel field measurements, examine major controlling variables, and develop a conceptual biogeochemical model for greenhouse gases at the top of a well-controlled landfill.

## MATERIALS AND METHODS

### Description of Field Site

Two experimental sites were established at the Mallard Lake Landfill, DuPage County, Illinois. Because our previous transect studies (Bogner et al., 1993, 1995a) had determined that location relative to gas recovery wells was a major control on emissions, semipermanent *proximal* (adjacent to gas well) and *distal* (between well) subsites were established for longer-term observation of proximal-distal differences. Our purpose was not to characterize whole landfill emissions but to examine controlling variables through temporal data collection. Final soil cover was placed over the refuse in 1989. The cover is 125 to 150 cm thick, consisting of locally recycled silty clay diamicton (late Wisconsinan Wadsworth Formation) overlaid by replaced "topsoil" (mollic epipedon of local mollisols, approximately 25 cm thick). Vegetative cover is 100%, consisting of mixed grasses with some native species and weedy invaders. No supplemental irrigation or fertilization is practiced. The site has a pumped gas recovery system with vertical wells to reduce emissions and recover CH<sub>4</sub> for commercial use (electrical generation). Additional description of the field site; the physical, chemical, and microbiological properties of cover soils; preliminary investigations; details of field and laboratory methods; and the kinetics of methane oxidation have been previously published (Bogner et al., 1993; 1995a,b; 1997a).

We also measured fluxes at two "control" sites: a non-landfill control site at Argonne National Laboratory with similar soils, and an adjacent landfill subsite undergoing rapid subsidence. The use of a non-landfill control near Mallard Lake was ruled out because of intensive suburban development in recent years and extensive re-grading in forest preserve areas adjacent to the landfill. The natural soils at the Argonne site (mollisol over silty clay diamicton parent material) are similar to the replaced soils at the Mallard Lake landfill. Moreover, the Argonne area has been infrequently fertilized since original seeding in the 1960s. The second control was implemented during October 1995, in a major settlement depression developing between the distal and proximal locations. We hypothesized that the observed settlement basin more than 1 m deep was the site of accelerated decomposition and higher methane fluxes, approaching a "worst case" condition for the study site.

### Field Methods and Gas Analysis

Soil gas concentration profiles for CH<sub>4</sub>, CO<sub>2</sub>, N<sub>2</sub>O, O<sub>2</sub>, N<sub>2</sub>, and Ar using paired permanent probes were determined in parallel with emission rates using static enclosure (chamber) techniques during July through December 1995. Chambers consisted of stainless steel hemispheres with gas sampling ports that were matched with semipermanent iron collars, as previously described (Bogner et al., 1997a). Probes were constructed of 1.3 cm o.d. chlorinated polyvinyl chloride with gas-tight top fittings. Soil gas analyses were completed by using a multiple gas chromatography system at Argonne National Laboratory customized for landfill gas applications (four inter-

plumbed gas chromatographs with six columns and six detectors) as previously described (Bogner et al., 1997a; Spokas and Bogner, 1996). All gases were individually calibrated by using external standards; the system had a repeatability of  $\pm 1\%$  and an absolute accuracy of  $\pm 5\%$ .

Both the proximal and distal subsites included paired collars for periodic placement of chambers and paired sets of soil gas probes ranging in depth from 10 to 165 cm. The bottom end of each probe was capped, and a series of side holes were drilled around the probe diameter. Each probe was placed in an individual augered hole, backfilled with pea gravel around the perforated interval, and then sealed with wetted bentonite to the ground surface. Parallel monitoring was implemented for air temperature, shallow soil (10 cm) temperature, and near-surface (0–10 cm) gravimetric soil moisture. Temperatures were monitored using thermister probes traceable to National Institute of Standards and Technology standards; gravimetric soil moisture was determined by overnight weight loss at 105°C. Except for overnight monitoring during a mid-October shutdown and restart of the gas recovery system, both the chamber fluxes and determination of vertical concentration gradients were done weekly at the same time of day (midmorning) to minimize diel variations.

For each flux measurement, the chamber was seated firmly into a trough at the top of the collar using hand clamps and a water seal. Samples were simultaneously taken from each of two adjacent paired chambers at 0, 10, 20, and 30 min. Over short monitoring periods ( $\leq 30$  min), this method yields a direct measure of gaseous flux from a soil surface when a short time ( $t$ ) series of concentrations ( $c$ ) is obtained, and the positive sloped  $dc/dt$  is multiplied by the volume/area ratio of the chamber (19 L/1134 cm<sup>2</sup>). The plots were well-described by a linear model; an acceptance criterion of  $r^2 \geq 0.8$  for the linear regression of  $dc/dt$  was applied to all measured fluxes. As originally described by Whalen and Reeburgh (1990) for tundra settings, the static chamber can also function in reverse to examine the net uptake (oxidation) of atmospheric methane under the chamber. In such cases, the slope for  $dc/dt$  is negative. Samples were removed using gas-tight glass syringes flushed with 10 volumes of air and retained for transport in small (11 mL) customized stainless steel containers that were pre-evacuated in the laboratory and then overpressurized with sample gas. Each reported flux is the average of two to six replicates (one to three sets of paired chamber measurements).

## RESULTS AND DISCUSSION

### Measured Emissions and Major Controls

Table 1 summarizes measurements of CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>O emissions from static chambers. Time-series plots for the three fluxes (CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>O), soil temperature, and soil moisture are given in Fig. 1. For CH<sub>4</sub>, both the proximal and distal fluxes were consistently negative, even into winter conditions, indicating net consumption of atmospheric CH<sub>4</sub>. This consumption is attributed to high capacities for CH<sub>4</sub> oxidation in soils with significantly reduced CH<sub>4</sub> compared with previous years, the result of optimization of the pumped gas recovery system during the period of 1994–1995 (Bogner et al., 1995a, 1997a). Using the absolute value of the negative fluxes as a measure of the rate of atmospheric methane oxidation (Whalen and Reeburgh, 1990), it can be seen that the average absolute rates were higher for the distal over the proximal area. This is attributed to

**Table 1. Summary statistics for measured fluxes using static chambers.**

	Negative methane†	(DRSPC) Carbon dioxide‡	Nitrous oxide	Temperature, °C	
				Air	Soil
g m <sup>-2</sup> d <sup>-1</sup>					
<b>Proximal</b>					
Mean	6.81 × 10 <sup>-3</sup>	8.94	8.34 × 10 <sup>-4</sup>	14.3	15.0
Minimum	4.07 × 10 <sup>-4</sup>	0.92	9.04 × 10 <sup>-5</sup>	-14.0	Frozen
Maximum	4.33 × 10 <sup>-2</sup>	31	3.01 × 10 <sup>-3</sup>	30.0	28.9
SD	1.15 × 10 <sup>-2</sup>	8.79	8.95 × 10 <sup>-4</sup>	11.4	8.9
N	22	26	21	24	24
<b>Distal</b>					
Mean	1.05 × 10 <sup>-2</sup>	22.4	1.80 × 10 <sup>-3</sup>	16.2	16.6
Minimum	6.67 × 10 <sup>-4</sup>	2.55	2.02 × 10 <sup>-4</sup>	-25.1	Frozen
Maximum	9.19 × 10 <sup>-2</sup>	58.7	8.55 × 10 <sup>-3</sup>	32.2	29.4
SD	2.00 × 10 <sup>-2</sup>	15.9	1.92 × 10 <sup>-3</sup>	12.6	10.6
N	25	27	24	29	29

† All CH<sub>4</sub> fluxes were negative (e.g., net oxidation of atmospheric CH<sub>4</sub>) with the exception of one initial positive value of 4.45 × 10<sup>-3</sup> (proximal, omitted in summary table above).

‡ Carbon dioxide is measured as the dark respiration of the soil-plant community (DRSPC).

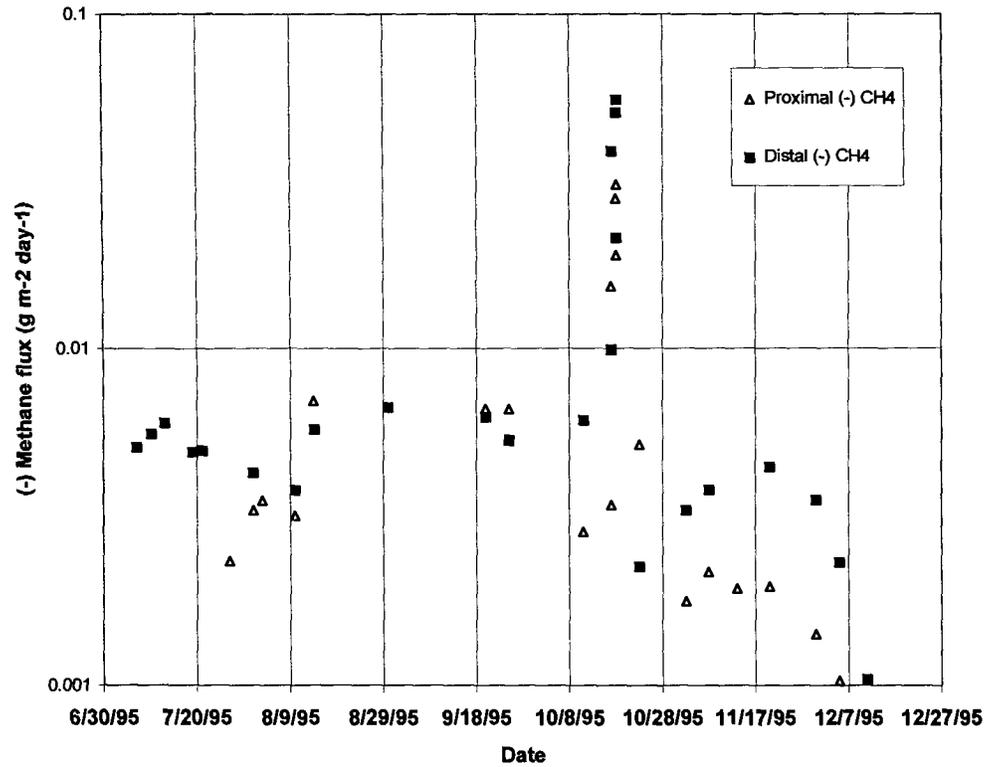
a combination of the diminished influence of the gas recovery system on reducing near-surface CH<sub>4</sub> mixing ratios in the distal area with higher methane oxidation rates in response to higher methane-mixing ratios. The high negative methane fluxes during mid-October 1995 (Fig. 1a) resulted from a rapid oxidation response to increased methane during a 2-d period when the gas recovery system was disabled. More intensive monitoring was conducted during this period to quantify the oxidation rate response to the shut down and subsequent restart of the pumped system (Bogner et al., 1997a). In this complementary work (Fig. 3 and 4, Bogner et al., 1997a), when all proximal and distal data were composited, the rate of CH<sub>4</sub> oxidation (negative flux) was highly correlated to the initial chamber CH<sub>4</sub> mixing ratio, as a direct response approximating Michaelis-Menten kinetics. Moreover, the rates of CH<sub>4</sub> oxidation from parallel field incubation studies clustered with the negative chamber fluxes in kinetic plots (Bogner et al., 1997a). Historical site records suggest that other periods of higher negative CH<sub>4</sub> flux (e.g., mid-September) were also related to shutdowns of short duration.

The average fluxes of CO<sub>2</sub> and N<sub>2</sub>O were in ranges similar to nonlandfill soils in temperate climates. Carbon dioxide is produced and consumed in many soil and plant processes; correspondingly, numerous approaches exist for quantification of various CO<sub>2</sub> fluxes within the soil-plant system (see discussion in Panikov and Gorbenko, 1992). In this study, the use of opaque static chambers measured the dark respiration of the soil-plant community (DRSPC), or the net CO<sub>2</sub> production from root zone respiration without photosynthetic consumption. In nonlandfill soils, the DRSPC is strongly dependent on temperature, reflecting increased soil microfaunal and macrofaunal activity at higher temperatures. Carbon dioxide fluxes also undergo both diel and seasonal cycles relative to temperature; the cycles may be similar in widely separated locations with the same seasonality (Panikov and Gorbenko, 1992). Our landfill values (Table 1), ranging from 0.92 to 58.7 g m<sup>-2</sup> d<sup>-1</sup>, compared favorably to the DRSPC of a Russian forest soil (0.88–22.0 g m<sup>-2</sup> d<sup>-1</sup>, Panikov and Gorbenko, 1992) and a California sandy loam (7.9–19.6 g m<sup>-2</sup> d<sup>-1</sup>, Simu-

nek and Suarez, 1993; Suarez and Simunek, 1993). For Mallard Lake, the higher distal maximum is largely attributed to higher seasonal heating associated with its location on a south-facing slope. Because CO<sub>2</sub> is produced in equimolar quantities to CH<sub>4</sub> consumed, we would suggest that there is also a contribution at the distal site from methane oxidation. However, in spite of steep distal soil gas methane gradients, no net methane emissions were measured at the surface, suggesting high in situ capacities for oxidation. For the proximal location, the production of CO<sub>2</sub> from CH<sub>4</sub> oxidation would not be a significant input to the observed CO<sub>2</sub> flux (<1%). As seen in Fig. 1b, both proximal and distal locations showed declining CO<sub>2</sub> fluxes parallel to declining temperature (Fig. 1d), especially during the period after 30 August. Moreover, CO<sub>2</sub> fluxes also declined during the mid-October shutdown when the surface was temporarily flooded by large volumes of methane passively venting from a non-operational flare. Composited CO<sub>2</sub> flux data (proximal plus distal) shows an exponential dependence on temperature over the monitoring range (Fig. 2), increasing slowly as temperature rose to 20°C and rapidly thereafter for small temperature increments. It should be kept in mind that the high "apparent" Q<sub>10</sub> indicated here for composited data results from higher distal CO<sub>2</sub> flux contributions from methane oxidation as well as root zone respiration.

Literature on N cycling and N<sub>2</sub>O fluxes in natural soils is vast (e.g., Firestone and Davidson, 1989; Davidson, 1991; Mosier et al., 1991). Emissions of N<sub>2</sub>O have been reported over a very wide range of values, approximately 3.0 × 10<sup>-7</sup> to 0.3 g m<sup>-2</sup> d<sup>-1</sup> (Rosswall, 1976; Rolston et al., 1976; Ryden et al., 1978; Hutchinson and Mosier, 1981; Smith et al., 1994). Variability is high, even within individual sites, with the highest values associated with wetter soils with large N input, particularly fertilized or manured fields (see Borjesson and Svensson, 1997b for discussion of N<sub>2</sub>O fluxes in landfill soil with high N input from sewage sludge). In this study, we do not attempt to address the entire soil N cycle but only examine likely mechanisms for the observed N<sub>2</sub>O production and emissions. At Mallard Lake, where no fertilization was practiced, values ranged from approximately 9.0 × 10<sup>-5</sup> to 9.0 × 10<sup>-3</sup> g m<sup>-2</sup> d<sup>-1</sup>, in the middle range of the soil values. As will be discussed below with the soil gas profile data, the average N<sub>2</sub>O flux was higher in the distal area. We attributed this difference to decreased aeration (lower soil gas O<sub>2</sub>) in the lower portion of the cover with higher rates of N<sub>2</sub>O production from denitrification. Overall, indigenous N was relatively high, with Kjeldahl N averaging 1700 (± 570) mg N kg<sup>-1</sup> dry soil in the replaced topsoil and 650 (± 60) mg N kg<sup>-1</sup> dry soil in the compacted clay below (Bogner et al., 1995b). As shown in Fig. 1c, a gradual declining trend for N<sub>2</sub>O fluxes was interrupted during the mid-October shutdown; at this time, a downward spike occurred in the distal area while an upward spike occurred in the proximal area. We suggest that changing aeration status at the 50 to 100 cm depth during this period is reflected in altered N<sub>2</sub>O production and the opposing flux trends. For the distal area, the rapidly increasing soil gas methane at the 50 to 100 cm depth retarded

a.



b.

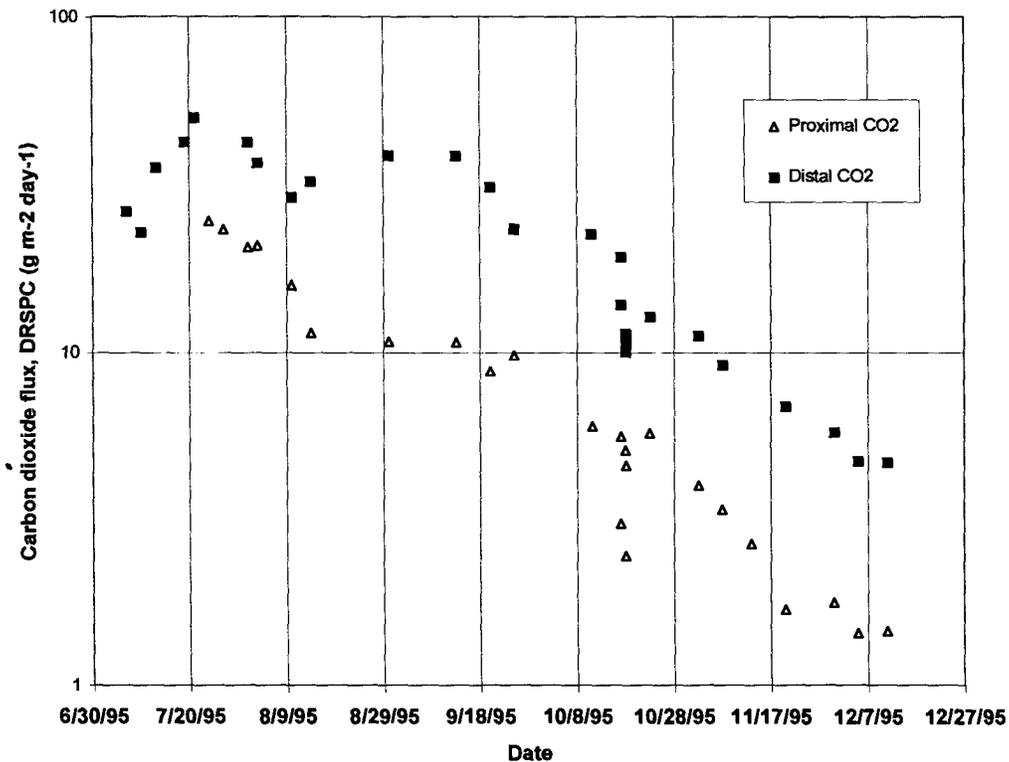
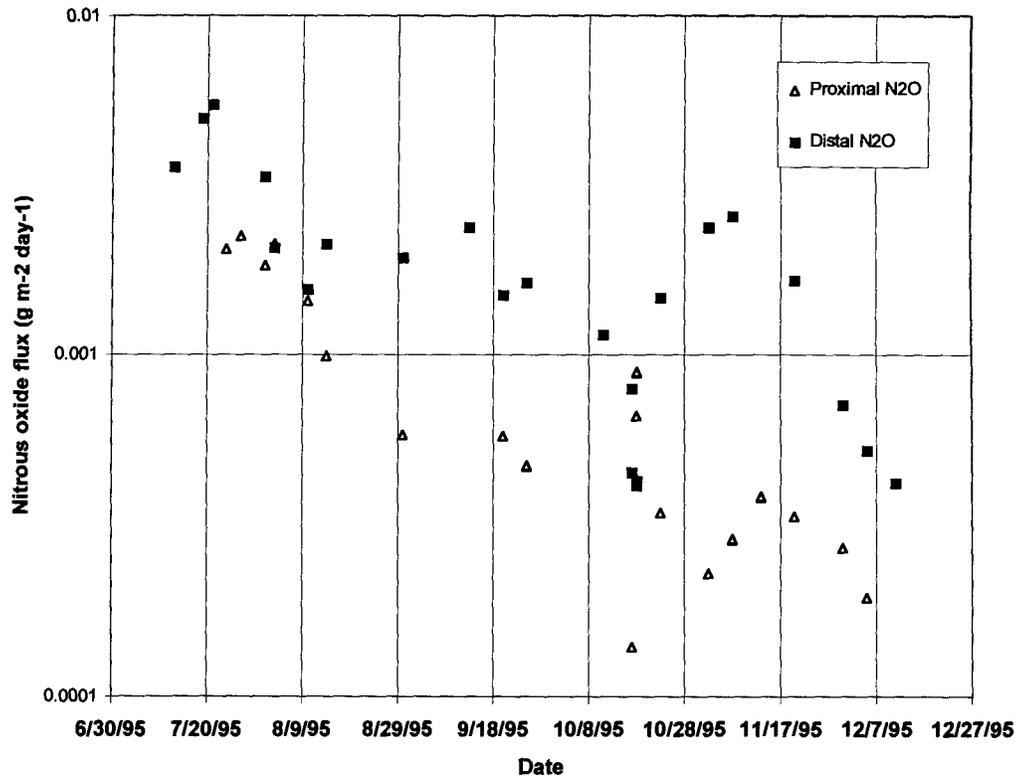


Fig. 1. Temporal variations in fluxes, soil temperature and soil moisture. All fluxes expressed as  $\text{g}(\text{gas}) \text{ m}^{-2} \text{ d}^{-1}$ . Data for mid-October 1995 are inclusive of overnight monitoring during shutdown and restart of gas recovery system. (a) Negative  $\text{CH}_4$  flux. Three point moving average. (b)  $\text{CO}_2$  flux as the dark respiration of the soil-plant community (DRSPC). Three point moving average. (c)  $\text{N}_2\text{O}$  flux. Three point moving average. (d) Soil temperature,  $^{\circ}\text{C}$  (10 cm). (e) Soil moisture, wt/dry wt. (%), 0 to 10 cm.

c.



d.

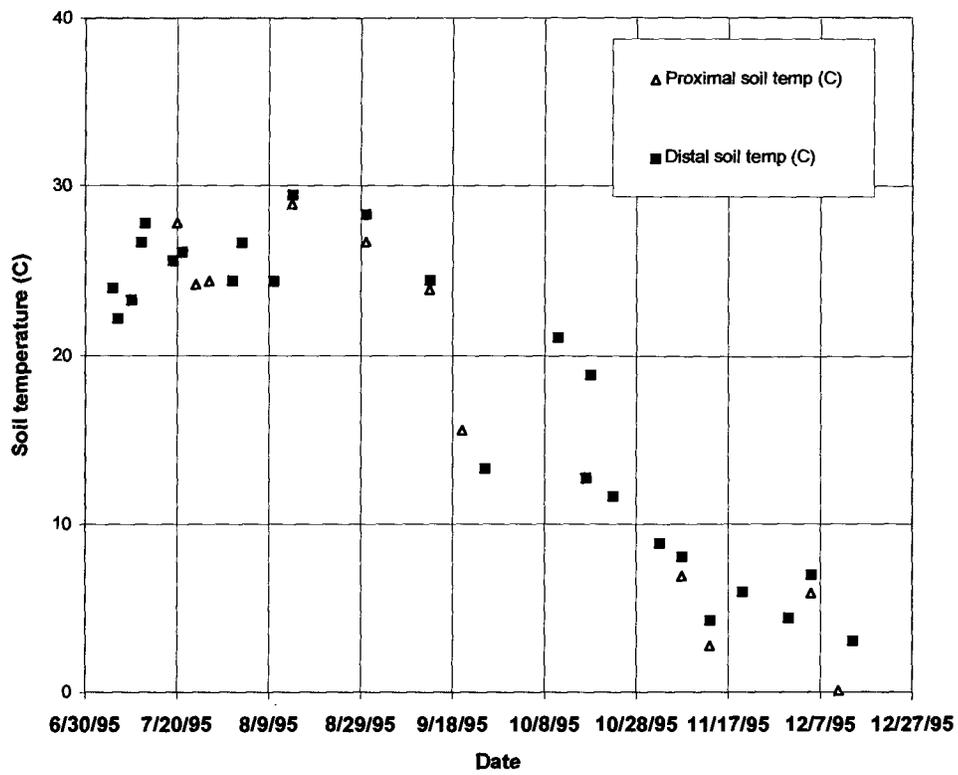


Fig. 1. Continued.

e.

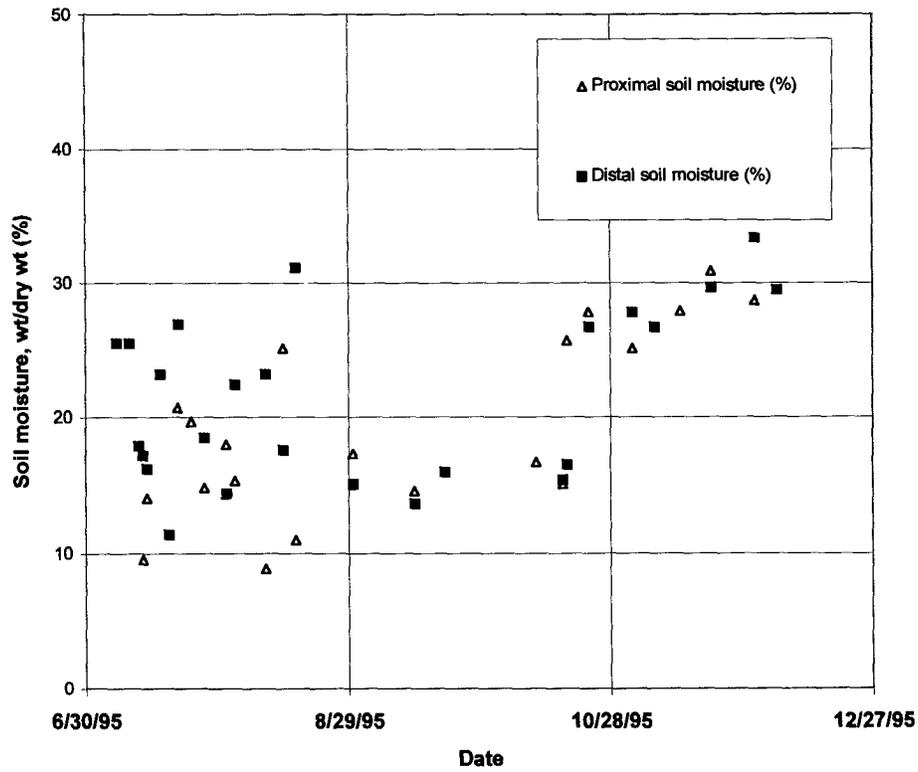


Fig. 1. Continued.

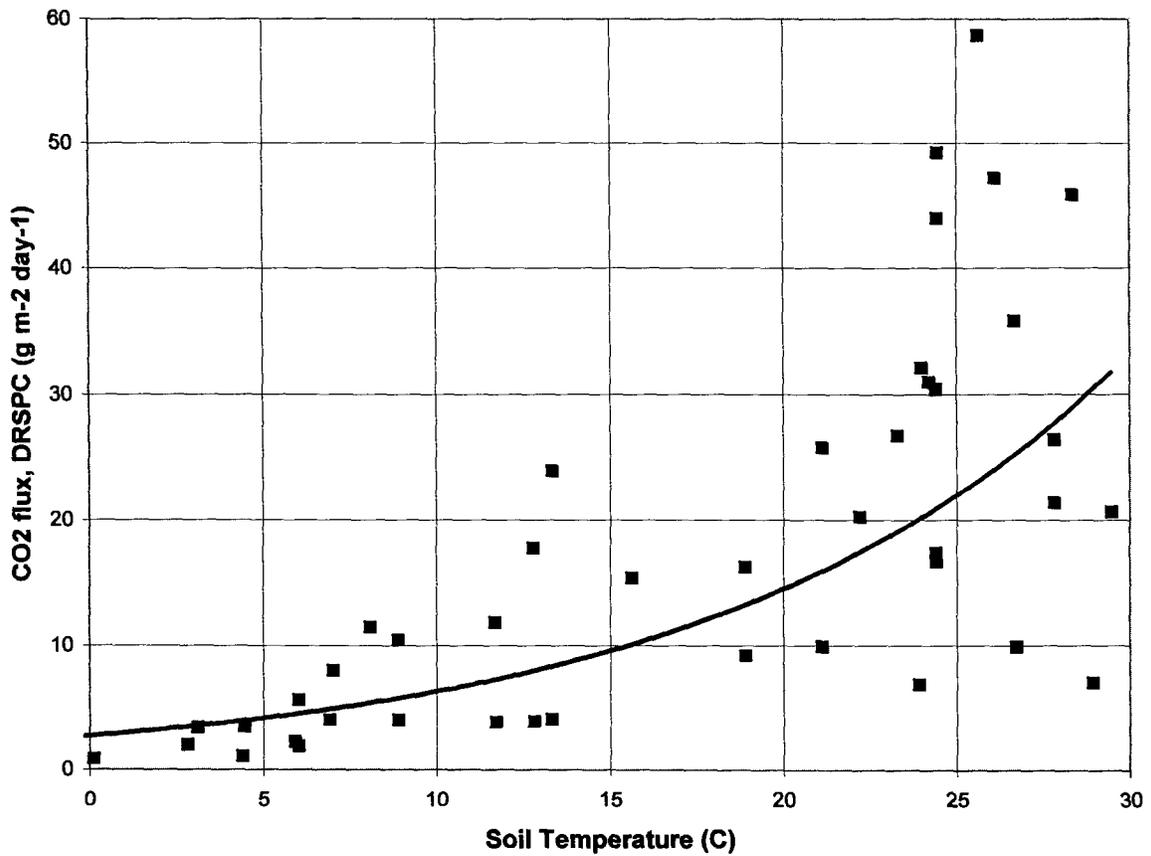


Fig. 2. Relationship between temperature and CO<sub>2</sub> flux (DRSPC) with all data combined. Fitted curve corresponds to  $y = 2.762 e^{0.083x}$  ( $r^2 = 0.614$ ).

N<sub>2</sub>O production due to temporary anaerobiosis. In the proximal area, where the lowest measured O<sub>2</sub> at 100 cm during the shut down was 15.9% by volume, N<sub>2</sub>O production was increased at this depth as aeration was decreased (soil gas mixing ratios similar to the distal site during normal operation of the gas recovery system).

In general, the highly variable data from the mid-October period reflect both the soil gas response to nonsteady state operation of the gas system and diel variations (fluxes measured five times over a 2-d period). Examining temporal trends for (negative) CH<sub>4</sub> and N<sub>2</sub>O fluxes (Fig. 1a,c), the high values in some cases were synchronous. The observed apparent synchronicity between high (negative) CH<sub>4</sub> and N<sub>2</sub>O fluxes in the proximal area during the mid-October shut down is believed to be related to a combination of increased rates of CH<sub>4</sub> oxidation responding to higher surface methane mixing ratios and higher N<sub>2</sub>O flux resulting from increased denitrification in the lower soil profile. As will be discussed below, methane oxidation is optimized near the soil-atmosphere interface while N<sub>2</sub>O production is optimized at greater depth.

For comparison with the landfill fluxes, two types of control measurements were implemented, as discussed above. First, a triplicate set of control fluxes using the same techniques were completed on a grassy lawn area at the Argonne site when the surface was saturated following more than 5 cm of precipitation over 48 h (November 1995). Because methanogenesis can occur within a few days of saturation in normally-aerated soils, a positive CH<sub>4</sub> flux might be expected and, indeed, averaged  $5.6 \times 10^{-3} \text{ g m}^{-2} \text{ d}^{-1}$ . The DRSPC averaged  $8.1 \text{ g m}^{-2} \text{ d}^{-1}$  while the N<sub>2</sub>O flux averaged  $4.6 \times 10^{-4} \text{ g m}^{-2} \text{ d}^{-1}$ . The low positive CH<sub>4</sub> flux approached the lowest positive values around  $10^{-4} \text{ g m}^{-2} \text{ d}^{-1}$  ever recorded in landfill settings (Bogner et al., 1997b) or wetlands (Bartlett and Harriss, 1993). Such values appear to represent a dynamic minimum for terrestrial settings where microbial CH<sub>4</sub> production and consumption both occur at a given site.

Toward the end of the monitoring period (October and November 1995), as a second control, fluxes also were measured at the settlement depression located between the proximal and distal areas. This was an area undergoing active subsidence with assumed high rates of localized methane generation and thus higher rates of methane flux to the atmosphere. Again, except for two occasions, all of the methane fluxes were negative, averaging  $8.53 \times 10^{-4} \text{ g m}^{-2} \text{ d}^{-1}$  with a high standard deviation ( $2.90 \times 10^{-4}$ ). The two exceptions (of nine monitoring events) were both times of high soil moisture contents (26–30%): the maximum positive flux was  $1.84 \times 10^{-2} \text{ g m}^{-2} \text{ d}^{-1}$ . At that time, the methane oxidation was assumed to be aeration-limited due to high surface moisture contents; however, we did not have complementary probe installations to confirm this.

Major controls on gaseous flux rates were investigated as the basis for preliminary model development. Because the gases of interest are microbially produced and consumed, temperature and moisture would be expected to be major influences. Soil organic matter, tem-

perature, and moisture have been shown previously to be major controls on CH<sub>4</sub> oxidation (Czepiel et al., 1994, 1996; Bender and Conrad, 1994; Boeckx and Van Cleemput, 1996; Borjesson and Svensson, 1997c). The organic matter content of the replaced topsoil and compacted clay was relatively high and uniform across the site, averaging 3.5% organic C in the topsoil and 1.6% in the compacted clay below (Bogner et al., 1995b). As shown in Fig. 1d and 1e, July to August 1995 was characterized by high surface soil temperatures and variable moisture content (24–30°C with moisture from 10–25%, wt./dry wt.), while September–November 1995 was characterized by steadily decreasing temperatures and increasing moisture until the time of ground freezing (temperatures of 5–15°C with moisture of 15–35%). Simple Pearson correlation coefficients for the three fluxes and a suite of potential controlling variables indicated that (i) the negative CH<sub>4</sub> fluxes were positively correlated with initial CH<sub>4</sub> concentration expressed as a mixing ratio ( $\mu\text{L L}^{-1}$ ), as a direct oxidation response ( $r = 0.99$ ); (ii) CO<sub>2</sub> and N<sub>2</sub>O fluxes were positively correlated with each other ( $r = 0.83$ ), a fortuitous relationship indicating common drivers (e.g., temperature); (iii) CO<sub>2</sub> flux was positively correlated with soil temperature ( $r = 0.73$ ); and (iv) gravimetric soil moisture and soil temperature were negatively correlated with each other for this period ( $r = -0.75$ ). Simple multiple linear regression equations for each flux [units of  $\text{g m}^{-2} \text{ d}^{-1}$ ] were developed by using an OLS (ordinary least squares) procedure that included the most significant variables from the initial analysis (highest Pearson  $r$ ) and selected soil gas mixing ratios ( $\mu\text{L L}^{-1}$ ). For the CO<sub>2</sub> and N<sub>2</sub>O fluxes, higher coefficients of determination were obtained when selected soil gas mixing ratios were included in the analysis (CO<sub>2</sub> at 25 and 50 cm depths for CO<sub>2</sub> flux; N<sub>2</sub>O at 100 cm depth for N<sub>2</sub>O flux; CH<sub>4</sub> at 100 cm depth for distal CO<sub>2</sub> flux). For the negative CH<sub>4</sub> flux, or net methane oxidation, the initial chamber mixing CH<sub>4</sub> mixing ratio was included (also see kinetic plots in Bogner et al., 1997a). The regression equations are:

1. [Negative] CH<sub>4</sub> flux = 0.00145 (initial CH<sub>4</sub> mixing ratio in chamber,  $\mu\text{L L}^{-1}$ ) – 0.00191 (soil moisture) + 0.0000999 (soil temperature) + 0.0037 ( $r^2 = 0.98$ ) (Proximal and distal data combined.)
2. Proximal CO<sub>2</sub> flux (DRSPC) = 0.005144 (CO<sub>2</sub> at 25 cm depth) – 0.000736 (CO<sub>2</sub> at 50 cm depth) + 0.367 (soil moisture) + 0.801 (soil temperature) – 17.6 ( $r^2 = 0.85$ )
3. Distal CO<sub>2</sub> flux (DRSPC) = –0.154 (CH<sub>4</sub> at 100 cm depth) – 0.000806 (CO<sub>2</sub> at 25 cm depth) + 0.000795 (CO<sub>2</sub> at 50 cm depth) + 6.42 (soil moisture) + 10.17 (soil temperature) – 261.8 ( $r^2 = 0.99$ )
4. Proximal N<sub>2</sub>O flux = 0.000203 (N<sub>2</sub>O at 100 cm depth) – 0.00000249 (soil moisture) + 0.0000353 (soil temperature) – 0.0003 ( $r^2 = 0.63$ )
5. Distal N<sub>2</sub>O flux = 0.000323 (N<sub>2</sub>O at 100 cm depth) – 0.0000328 (soil moisture) + 0.0000272 (soil temperature) – 0.0008 ( $r^2 = 0.76$ )

Soil gas profile data pertinent to these relationships will

be discussed in the next section. In addition, a conceptual model that encompasses a modified reduction sequence and suggests a zonation of major microbially driven soil gas processes will be introduced.

### Composite Soil Gas Profiles and Conceptual Biogeochemical Model

Composite profiles for the monitoring period were developed by plotting the geometric mean of probe

data (Bogner and Spokas, 1993; Bogner et al., 1993). Comparison of profiles for several gases is helpful to indicate vertical zonation of various processes and infer the direction of net diffusive fluxes following production and consumption processes. We also relied on soil gas Ar as a relative measure of changing aeration status, because Ar is an inert component of the atmosphere, averaging approximately 1V%.

Figure 3 shows the geometric mean profiles for  $\text{CH}_4$ ,  $\text{CO}_2$ , and  $\text{N}_2\text{O}$  with error bars representing 1 geometric

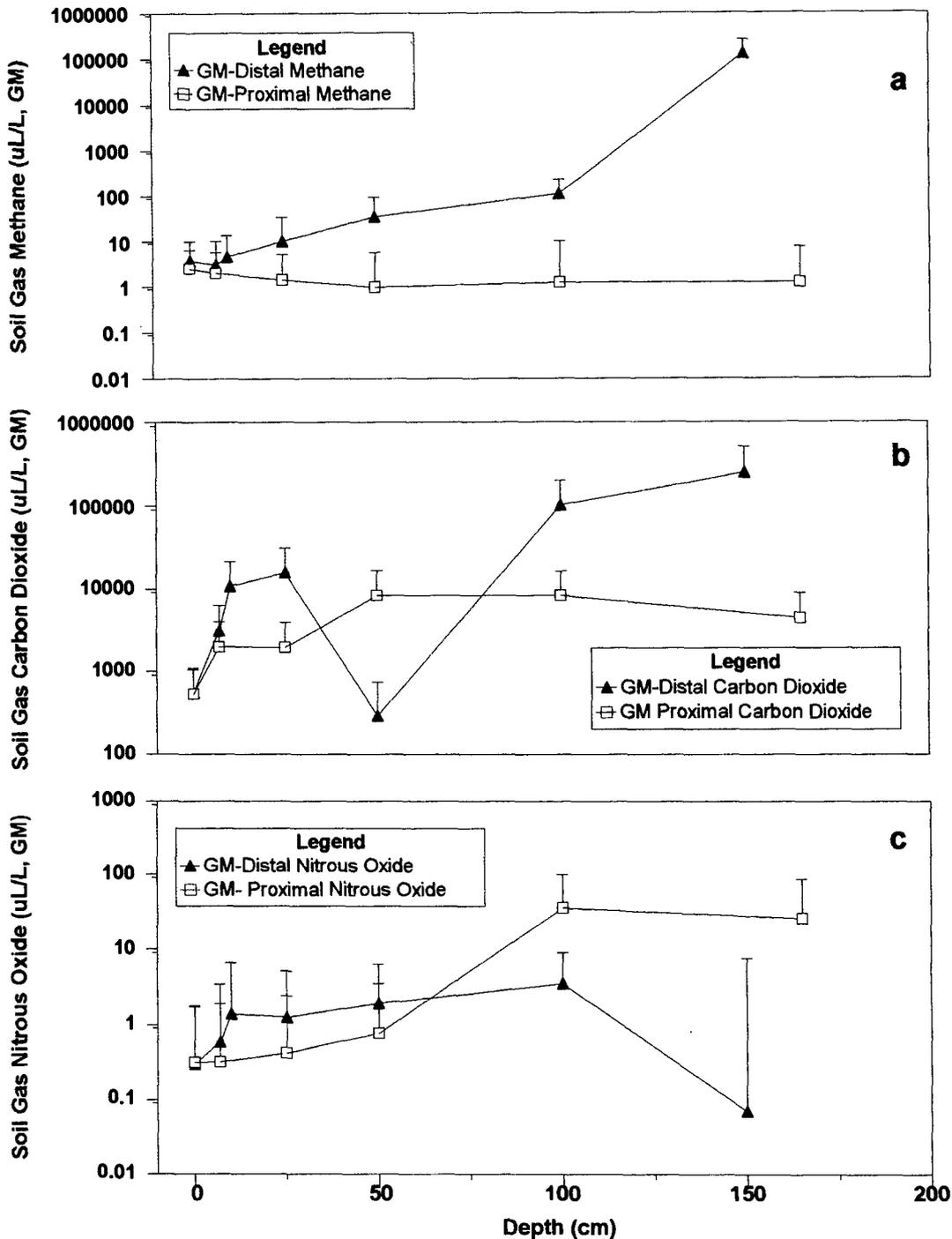


Fig. 3. Composite soil gas concentration profiles for  $\text{CH}_4$  (a),  $\text{CO}_2$  (b), and  $\text{N}_2\text{O}$  (c) at proximal and distal locations. Data are geometric mean concentrations. Error bars represent one geometric SD.

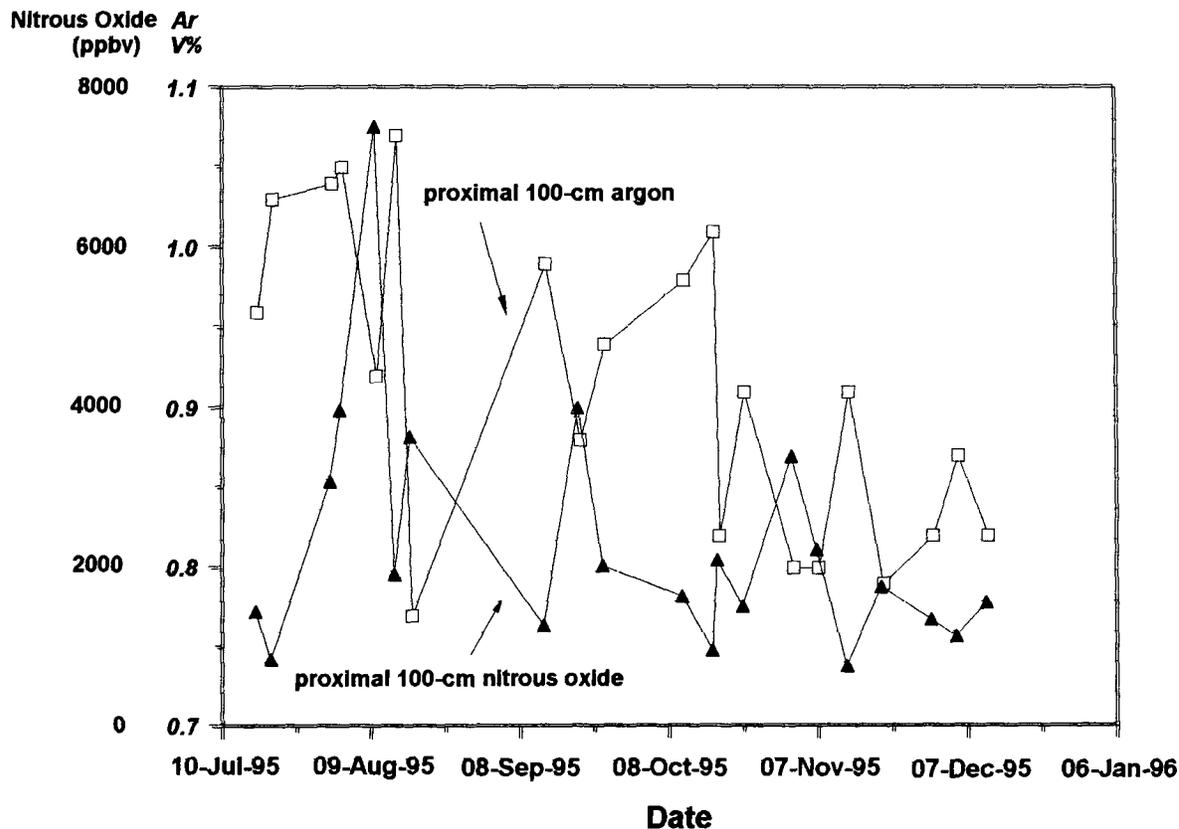


Fig. 4. Temporal variations in soil gas  $N_2O$  and Ar showing inverse relationship between restricted aeration (reduced atmospheric Ar) and increased  $N_2O$  at 100 cm depth.

SD. Proximal  $CH_4$  was uniformly low ( $1-2 \mu L L^{-1}$ ) to depths of  $>100$  cm; distal  $CH_4$  was low only in the surface  $CH_4$  oxidation zone, increasing about two orders of magnitude to more than  $100 \mu L L^{-1}$  at a depth of 100 cm. Both  $CH_4$  curves show a reversal in gradient at the depth of optimum  $CH_4$  oxidation (approximately 50 cm proximal, 7 cm distal). The general shapes of the  $CH_4$  curves were identical to those from a preliminary spring 1994 study but the distal mean value at 100 cm was higher in 1994 ( $1000 \mu L L^{-1}$ ). The  $CH_4$  curves for this study contrast with those for landfill sites with high rates of methanogenesis, low rates of oxidation, and no gas recovery; in such cases,  $CH_4$  may decrease more than four to five orders of magnitude between refuse production zones (nominally 50–60 V%  $CH_4$ ) to near atmospheric concentrations at the top of the cover (approximately  $1.7 \mu L L^{-1}$ ) (Bogner, 1992). At Mallard Lake, the negative  $CH_4$  flux rates responded to changing initial  $CH_4$  concentration (chamber air), indicating an oxidation response. Negative  $CH_4$  fluxes (net oxidation) have also been previously quantified at landfills in the USA, Sweden, and England (Bogner et al., 1997b and references cited therein).

With respect to  $CO_2$  (Fig. 3b), both the proximal and distal  $CO_2$  profiles show a "bulge" corresponding to the depth of optimum root zone  $CO_2$ . This bulge occurred at a depth of 50 to 100 cm for the proximal mean profile but at only 10 to 25 cm for the distal profile. Distal  $CO_2$  increased rapidly below 50 cm; the deeper distal profile mimics the corresponding  $CH_4$  curve, indicating diffu-

sive transport of both  $CO_2$  and  $CH_4$  from deeper methanogenic production zones and, as discussed above, deeper methane oxidation. Typically, soil gas  $CH_4$  mixing ratios are 50 to 60 V% in methanogenic production zones, with the remainder mostly  $CO_2$ . We suggest that the strong gradients for both  $CO_2$  and  $CH_4$  in the deeper cover soil at the distal location indicate a transport-dominated soil gas regime with some methane oxidation; as a result, root zone respiration is optimized higher in the soil profile. The proximal  $CO_2$  maximum at the 50 to 100 cm depth was low compared with local undisturbed mollisols (generally 2–3 V%, unpublished data). Also, in contrast to the distal curve, the proximal  $CO_2$  was steady to decreasing below 100 cm.

The geometric mean  $N_2O$  profiles (Fig. 3c) indicate a maximum at 100 cm. However, compared to  $CH_4$  and  $CO_2$ , the wider error bars for  $N_2O$  at several depths attest to the dynamic variability of  $N_2O$  production relative to changing soil moisture and aeration status. The  $N_2O$  concentrations at 100 cm were inversely correlated with soil gas Ar, indicating restricted aeration and increased  $N_2O$  production from denitrification (Fig. 4). Overall, the minimum  $O_2$  content of soil air at depths of 50 to 100 cm was approximately 11 V%, about half of the ambient air concentration.  $N_2O$  fluxes were linearly correlated with  $N_2O$  concentrations at the 100 cm depth with ( $r = 0.84$  distal and  $0.63$  proximal).

Temporal changes in soil gases were well separated by soil type, that is, the replaced topsoil curves (surface, 7, 10, and 25 cm) clustered together, while a separate

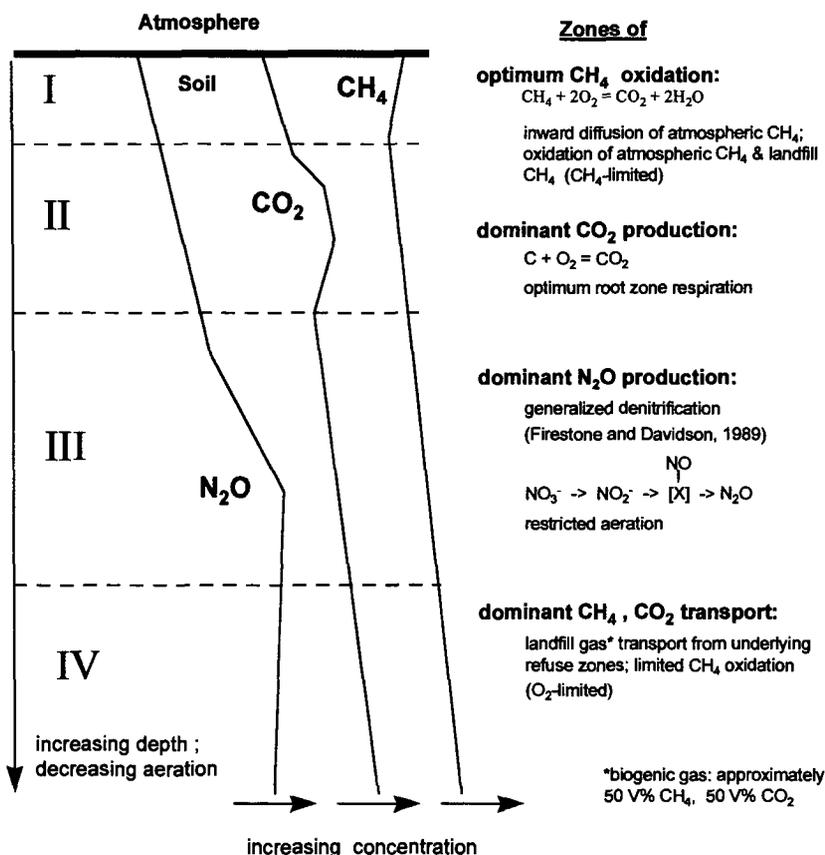


Fig. 5. Conceptual biogeochemical model for near-surface CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>O at landfill sites with gas recovery systems.

cluster of curves could be observed for the deeper compacted clay (not shown). This was especially true for the proximal location for CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>O. In general, the proximal curves were much less noisy than the distal curves, suggesting that the gas recovery system at depth has a significant moderating influence on fluctuations of soil gas concentrations for the proximal location. Given consistent gas system operation without shutdowns, the data further suggest that a relatively high degree of predictability for soil gas concentrations might be achieved.

In summary, Fig. 5 presents a conceptual biogeochemical model for landfill sites with gas recovery systems, which was developed from profile data and relationships discussed previously. Landfill cover soils function as a dynamic mixing zone for landfill and atmospheric gases, where the observed flux to the atmosphere is a function of both microbial production/consumption reactions and gaseous transport processes. The lowest zone (IV) is dominated by transport of landfill gas (CH<sub>4</sub> and CO<sub>2</sub>), with CH<sub>4</sub> oxidation limited by available O<sub>2</sub> from atmospheric sources (Bogner et al., 1997a,b). The depth of this zone is much shallower for the distal location, where large concentration gradients for both gases exist, representing the diminished influence of the gas recovery system. Zone III corresponds to optimum N<sub>2</sub>O production due to restricted aeration below or toward the base of the zone of optimum CO<sub>2</sub> production (Zone II), the zone of optimum root zone respiration. For the proximal site, because of improved aeration at depth, zone II

extends over a wider depth range. From geometric mean profiles at Mallard Lake, N<sub>2</sub>O appears to peak at about 100 cm depth, but this optimum depth varies over zones II to III because of seasonal changes in soil moisture and aeration status. Finally, an upper zone I is characterized by inward diffusion of atmospheric CH<sub>4</sub> and other gases (O<sub>2</sub>, Ar, and N<sub>2</sub>) and is a dominant zone for CH<sub>4</sub>-limited oxidation of both landfill and atmospheric CH<sub>4</sub> (Bogner et al., 1997a).

Direct field measurements are essential for improved understanding of landfill emissions and form the basis for model development based on an evolving geochemical framework. The modeling process for net CH<sub>4</sub> emissions has been initiated (Bogner et al., 1997a). Such models can assist with improved quantification of greenhouse gas emissions at representative sites and provide guidance for scaling up to national and global levels. More generally, this work shows that biogeochemical processes resulting from the relatively rapid development of a functional soil microbial ecology at disturbed sites can be recognized and quantified.

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