UNC Charlotte, Department of Civil and Environmental Engineering

Master Thesis Defense

IMMOBILIZED METHANOTROPH BIOTARP DESIGN FOR LANDFILL METHANE MITIGATION

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Global introduction

- **Methane**, carbon dioxide, and CFC's are the main **greenhouse gases** that contribute to global warming. Methane absorbs terrestrial infrared radiation **25 times** more effectively than carbon dioxide.

- Natural sources methane (30%) are wetlands, termites and ruminants, some forest soils, the oceans and freshwater sediment.

- Anthropogenic emissions constitute (70%) of total methane emissions: e.g. rice cultivation, animal feedlots and **landfills.**

- Methane emissions from landfills range from 0.0002 to 4000 g/m^2-day and contribute **8% of the global emissions.**

- Many landfills have **gas collection systems**. However, they recover about 90% of the methane produced beneath a geomembrane final cover and 65% of the methane beneath a temporary cover.

- On an open working cell, the EPA requires that **a daily cover of 6 in of soil be placed at the end of each working day** to prevent rodents from reaching the trash, debris from littering the surroundings, and odors from permeating surrounding areas.

- However, daily cover is not aimed at preventing **landfill gas from escaping into the atmosphere**.

The Biotarp Project

Goal: To reduce landfill methane emissions through use of a bioactive alternative daily cover

Phase I: Cell immobilization

Test several bacterial immobilization techniques and identify the three most promising in terms of (a) long term methane oxidation activity and (b) tolerance to varying environmental stressors.

Phase II: Tarp design

Design a tarp matrix that will physically support the immobilized cells and serve the function of an alternative daily cover.

Phase III: Field tests

Test prototype biotarp to assess performance under a variety of climate conditions.

Methanotrophic bacteria

- Methanotrophic bacteria are aerobes that **obtain both energy and carbon from methane**.
- Methane oxidation leads to the production of **CO_2** and **water vapor.**
- Methanotrophs are ubiquitous in the environment and can be **found in landfill cover soil**.
- Methanotrophs have been exploited in landfills with the use of different bio-based systems (biofilters, biowindows and biocovers) to mitigate methane emissions.

Alternative Daily Covers

- Alternative daily covers (ADCs) are substitutes for **the 6 in daily soil cover layers.**

- They can be made from **waste-derived materials**:
  Ash and cement kiln dust, shredded tires, compost, sludge, green material, contaminated sediments, treated auto shredder part, construction and demolition waste.

Often they are simply these materials mixed with some soil.

- On the other hand, they can be a **non-waste-derived product, such as foam, sprayed slurries, or fabric tarps.**

They save valuable landfill space if they compress readily or can be removed and re-emplaced each day.

Phase I Results

Phase I: Cell immobilization

- Among the several immobilization methods tested (adsorption, entrapment and encapsulation), **adsorption** proved to be simple and effective.

- A **variety of materials** such as geotextiles, natural sponge, glass beads, trickling filter and polycarbonate membrane were tested.

- The **sponge and geotextiles** performed best at supporting methane uptake under a 10% methane headspace.

Phase 2 Objectives

Objective 1: **Evaluate different geotextile materials** for their ability to support methanotrophs and a high methane uptake rate.

Objective 2: **Build a continuous flow chamber** that simulates the landfill conditions to assess maximum methane uptake achievable by different biotarp configurations.

Objective 3: Validate a sampling protocol for future **field tests.**

Materials and Methods

- Methanotrophic Bacteria

- Gas Chromatograph

- Geotextile Testing
  - Different types of Geotextile
  - Tests done on the Geotextiles

- Continuous Flow Experiments
  - Continuous flow chamber design
  - Inside frame design
  - Synthetic landfill gas flow
  - Sampling and analyzing

- Flux Chambers
  - Landfill site
  - Flux chamber design
  - Field protocol

Methanotrophic bacteria

- First isolated from some soil collected from **a closed landfill** converted to public soccer fields (Renaissance Park, Charlotte, NC).

- Various strength soil slurries were streaked onto Petri dishes containing Whittenbury's Nitrate Mineral Salts (NMS) agar media and incubated in an anaerobic jar under a 50% methane atmosphere.

- A liquid mixed culture of methanotrophs was developed and grown on NMS liquid media under a **10% methane headspace** in 100ml, 250ml or 2L flasks for 24 h at 300 rpm.

- Cultures were **centrifuged** and then **re-suspended** in fresh NMS before being applied to the geotextiles tested.

Gas Chromatograph

Methane, carbon dioxide, oxygen and nitrogen concentrations were monitored using a Shimadzu 14-A gas chromatograph (GC) equipped with a TCD, and an SRI GC equipped with a TCD and FID (for low methane concentrations).

Shimadzu GC-14A

SRI 8610C

Geotextiles Tested

Geotextile	Thickness (cm)	Color	Characteristics
20 osy wettable PP	0.81 ± 0.04	White	High water holding capacity
160N	0.30 ± 0.06	Black	Common geotextile: nonwoven geotextile composed of polypropylene fibers *
20 osy wettable PP 3 denier	0.97 ± 0.01	White	Version of 20 osy wettable PP with a lighter thread
6 osy wettable PP 3 denier	0.46 ± 0.04	White	Version of the 160N with a lighter thread
FR 60	0.36 ± 0.05	White	Textile treated with polyphosphate-based additive. **Releases inorganic phosphate when wetted.**
160N + FR 60	0.61 ± 0.05	White and Black	Composite of two geotextiles
30 osy PP	1.27 ± 0.01	White	thicker version of the 20 osy wettable PP
S1600	0.50 ± 0.01	Grey	Needle-punched nonwoven geotextile made of PP fibers, inert to biological degradation *
IR 26	0.70 ± 0.01	Black	High water holding capacity. One side of this geotextile is **fused during fabrication,** inducing a skin-like surface on one side.

Geotextile S1600

Geotextile 6 osy

*www.TenCate.com

Geotextile Assessments

Water holding capacity

Triplicate pieces of each geotextile were cut and then the following features were measured:

Weight of the tarp dry
Weight of the tarp drained
Weight of the tarp wrung out

Methane oxidation

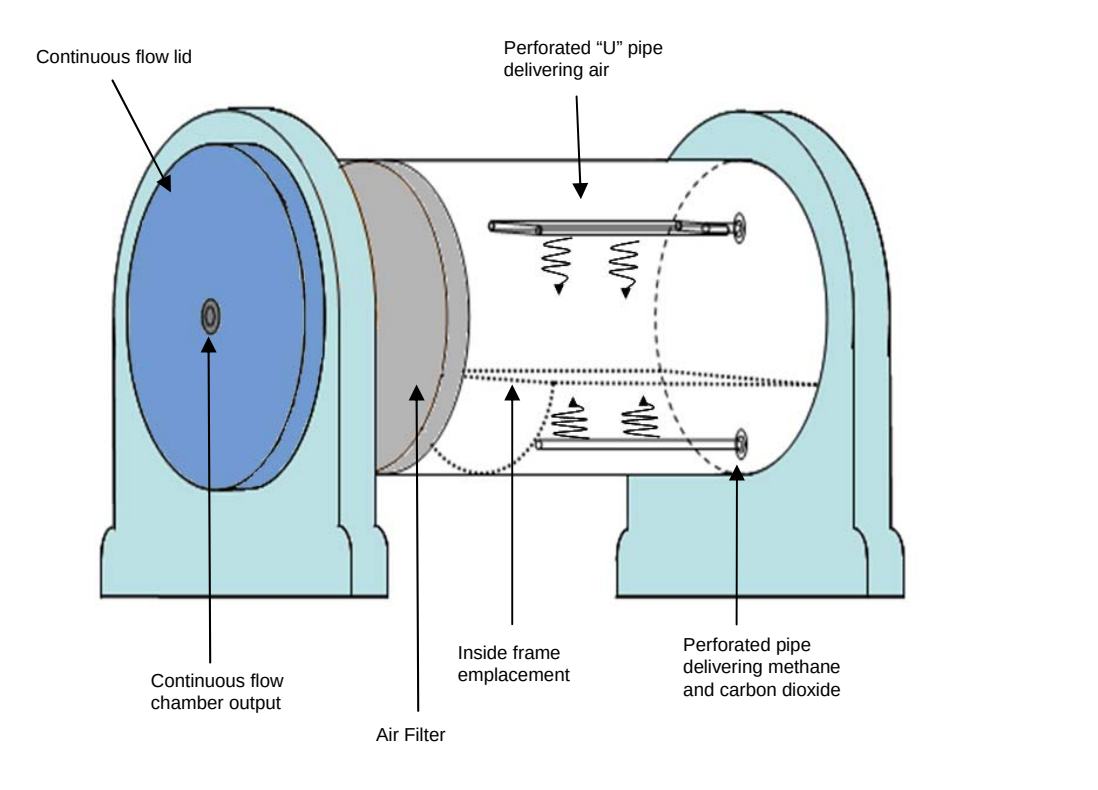
•Clean and sterile geotextile pieces were inoculated with **10 mL of freshly prepared mixed methanotroph culture.**

•The pieces were then tested in 100mL gas-tight bottles containing about **8% methane-in-air headspace**.

•Methane concentrations in the bottles were measured **initially and again after 24 h**

Continuous flow chamber design

- Continuous flow chambers were designed to **simulate landfill conditions.**
- Geotextile placed on **an inside frame.**
- Bottom tubing delivered a **synthetic landfill gas** mix to the chamber.
- Top U-shaped tubing delivered air.
- A circle sized filter ensured that gases from the chamber were well mixed prior to being sampled for analysis.

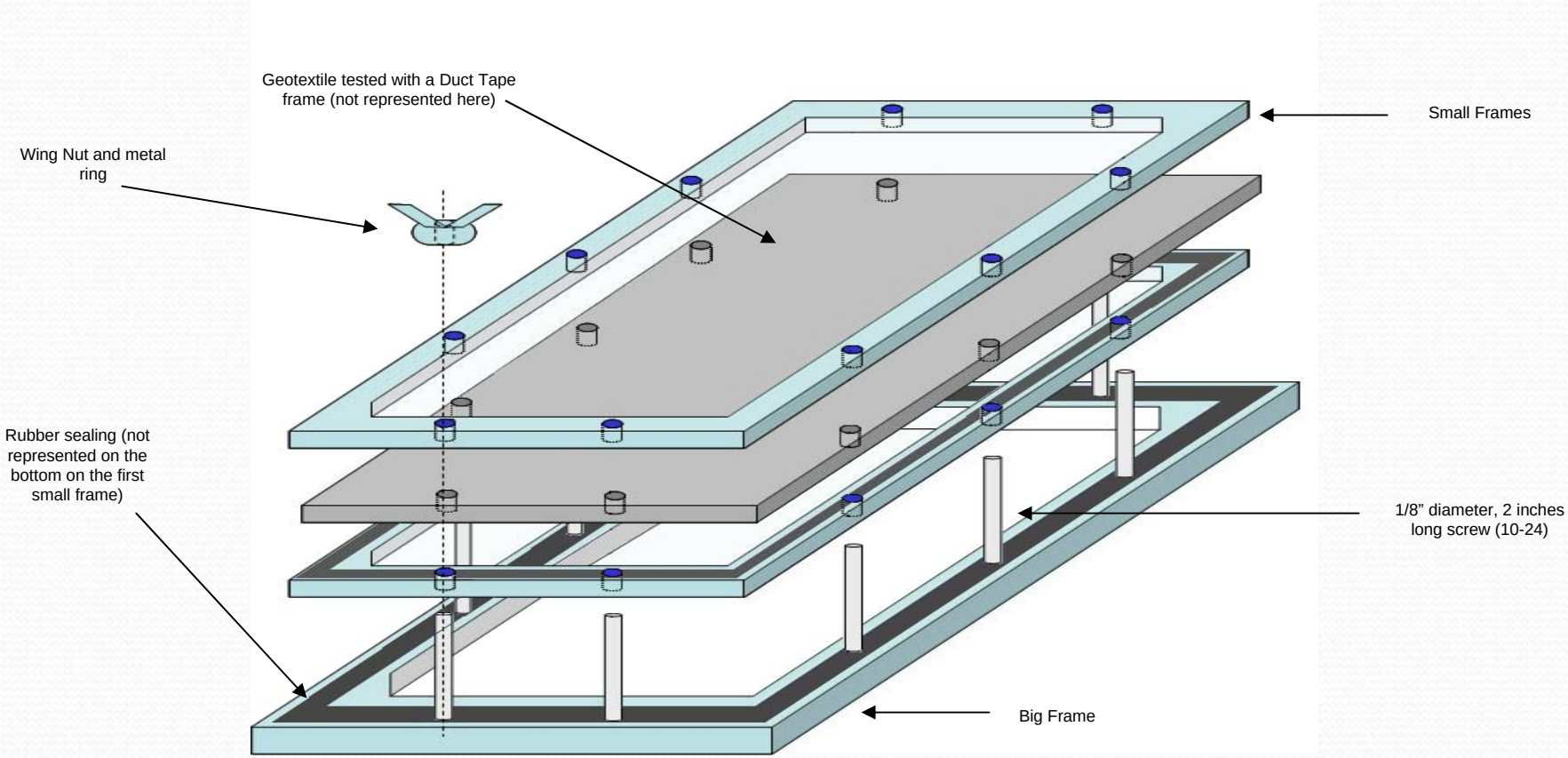


Inside frame

- Inside the bioreactor, a rectangular frame was installed to **hold the biotarp samples in place and prevent gas short-circuiting** during testing.

- The frames were stacked vertically with a biotarp sample in place, and the wing nuts were used to secure it.

- **Smoke tests** were performed to ensure no short-circuiting was occurring.



Synthetic landfill gas flow

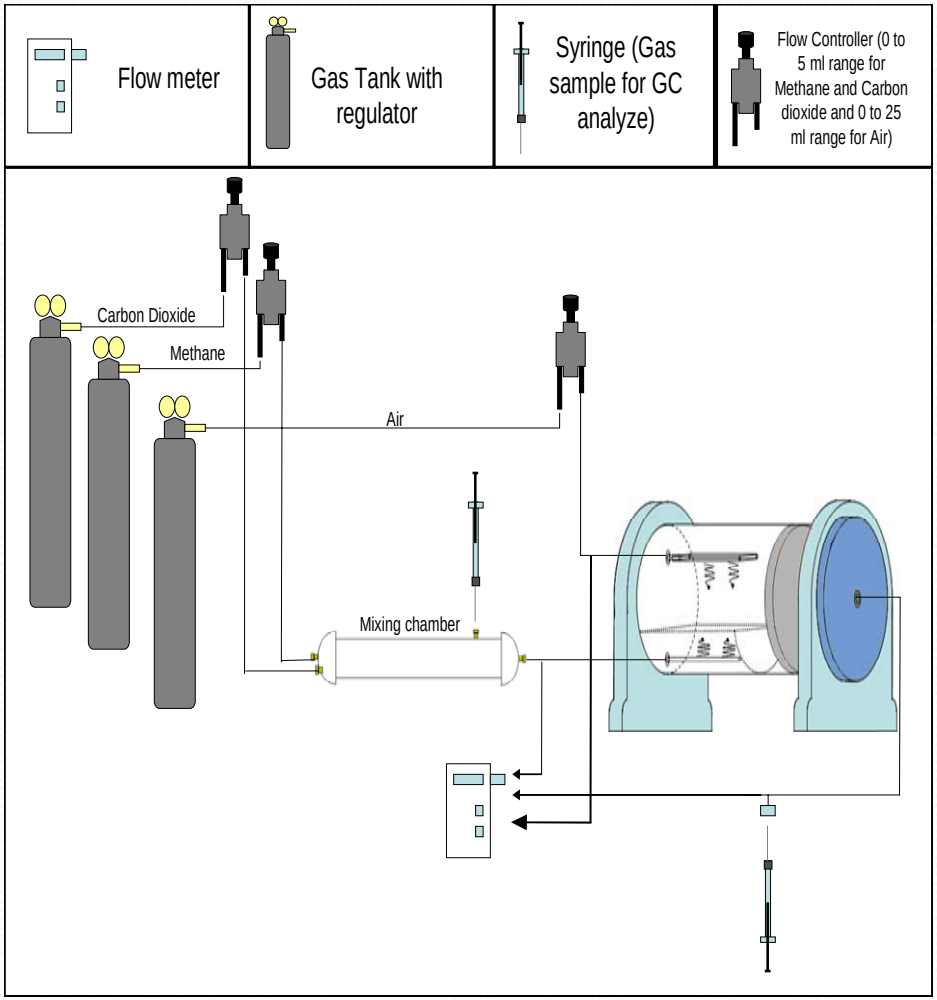
- The synthetic landfill gas was **50% methane and 50% carbon dioxide** and delivered at the bottom of the chamber.

- The gases were combined in a **mixing chamber** before entering the continuous flow chamber.

- **Air delivered at the top** of the continuous flow chamber was medical grade air.

- The flows were calibrated and monitored with a mass flow meter.

- The continuous flow chambers were operated to create a synthetic landfill gas flux of about **20-25 g m^{-2} d^{-1} of methane**.



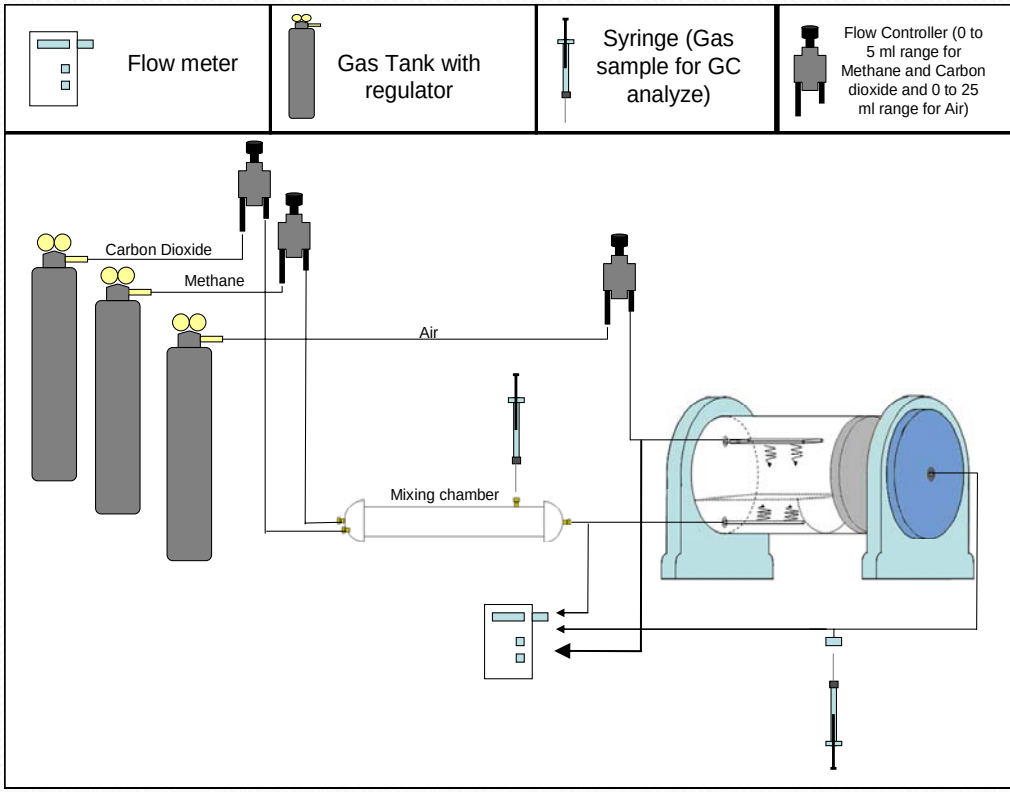
Sampling and Analyzing

- Analyzing the continuous flow chamber required measuring the **gas flows**:

  Mixing tube outflow to chamber , air inflow and chamber outflow (Flow meter)

- Measuring **gas concentrations** :

  Methane, carbon dioxide, oxygen and nitrogen (GC)



- and then performing a **mass balance analysis:**

$$\%CH_4 uptake = \frac{CH_4 in - CH_4 out}{CH_4 in} \times 100 = \frac{\%CH_{4in} \times Flow_{in} - \%CH_{4out} \times Flow_{out}}{Flow_{in} CH_{4in}} \times 100$$

Landfill site

- **Concord Motor Speedway (CMS) landfill** (Concord, NC), managed by Allied Waste Industries, Inc., provided an area on the landfill for the field chambers experiment.

- The site had about 2 ft of **intermediate cover** atop 1 year old municipal waste. The 2 ft depth of intermediate cover was composed of about 1 ft of clay topped by 1 foot of topsoil.

Flux chamber design

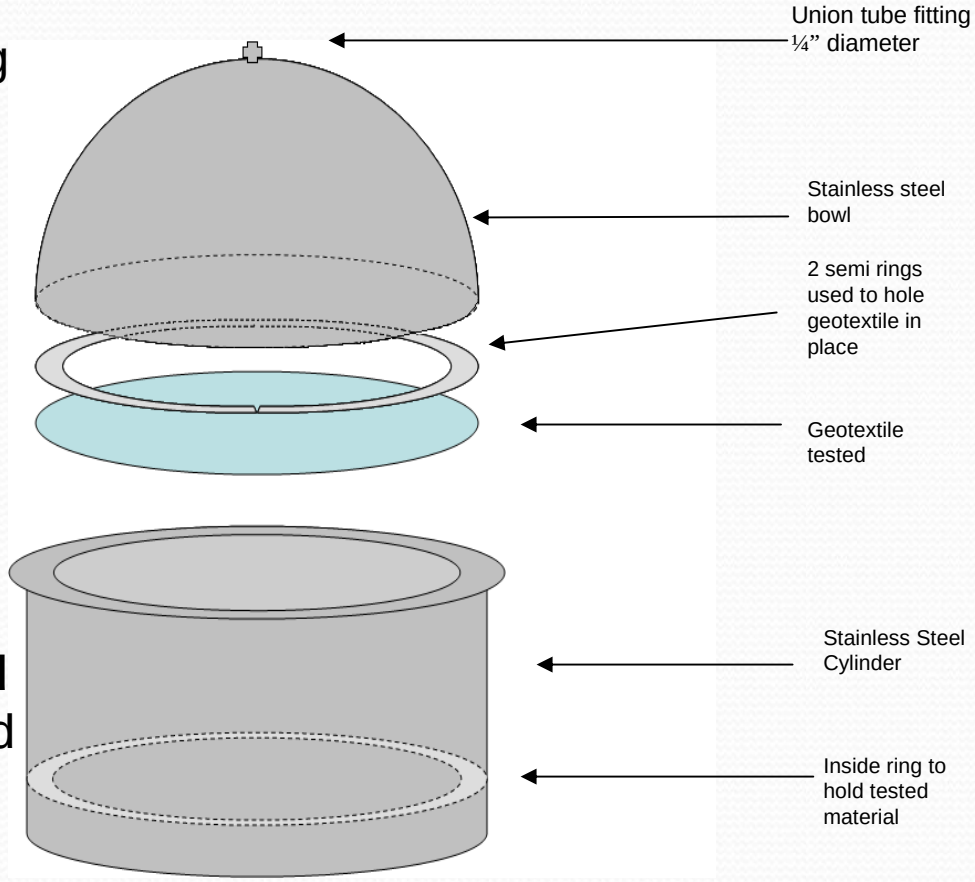
- The flux chambers were used to **measure the flux of methane** passing through the surface of a site where municipal solid waste was buried.

- Each chamber had two parts:

 -- a 16-in dia. stainless steel cylinder

 -- A stainless steel cover that fit into a channel on the base.

- The base and the top were **clamped together** and a water seal was poured at their interface.



Field protocol

- Samples were collected **every 5 min**. for **15 min in 60 ml plastic syringes .**
- The syringes were used to draw 50ml samples, which were injected into **20 ml evacuated vials**.
- After a session of sampling, the vials were analyzed using an SRI gas chromatograph **with FID.**
- A graph of the methane concentration versus time was plotted, and a **linear regression was applied.**
- The **slope** of the best fit line was used to calculate the methane mass flow rate from the soil in **ppm/min**.

This volumetric flux was converted to units of g/m^2-d with the following equation:

$$F = \frac{f * V}{1000} * \frac{P}{1000 * 1 * R * T} * 16 * \frac{1}{A} * 24 * 60$$

F is the methane flux in g/m^2-d
f is the methane flux in ppm/min
V is the flux chamber volume in m^3
P is the atmospheric pressure in Pa
R is the ideal gas law constant
T is the temperature in degrees Kelvin
A is the surface area of the flux chamber base in meters

Results / Discussion

- Batch Experiments
  - Water holding capacity
  - Methane uptake
  - Phosphorus release
- Continuous Flow Chamber Experiments
  - 1 layer geotextile
  - 2 layers geotextile
  - Multilayer geotextile
- Field-Scale Biotarp Tests
  - Bare refuse flux readings
  - Intermediate cover flux

Water holding capacity

	Manufacturer's Designation	Thickness (cm)	Dry tarp weight per m^2 (g/m^2)	Drained tarp weight per m^2 (g/m^2)	Wring out tarp weight per m^2 (g/m^2)
A	20 osy wettable PP	0.81	969 ± 20	7471 ± 451	4027 ± 114
B	160N	0.28	291 ± 2	955 ± 135	785 ± 28
C	20 osy wettable PP 3 denier	0.97	762 ± 38	3671 ± 290	1426 ± 48
D	6 osy wettable PP 3 denier	0.41	215 ± 24	2557 ± 193	1082 ± 117
E	FR 60	0.41	226 ± 13	2095 ± 124	796 ± 51
F	160N + FR 60	0.64	531 ± 12	3919 ± 196	1831 ± 105
G	30 osy PP	1.27	949 ± 58	7578 ± 553	4245 ± 215
H	S1600	0.50	720 ± 5	4461 ± 55	2999 ± 79
I	IR 26	0.70	1153	6812 ± 65	3976 ± 278

- Water holding capacity **varied widely among the geotextile**. Geotextile **A, G, H and I** had the best water holding capacity.
- This is a **good attribute in terms of methanotroph success,** but this also indicates that a possible biotarp made with these materials will be **heavy.**

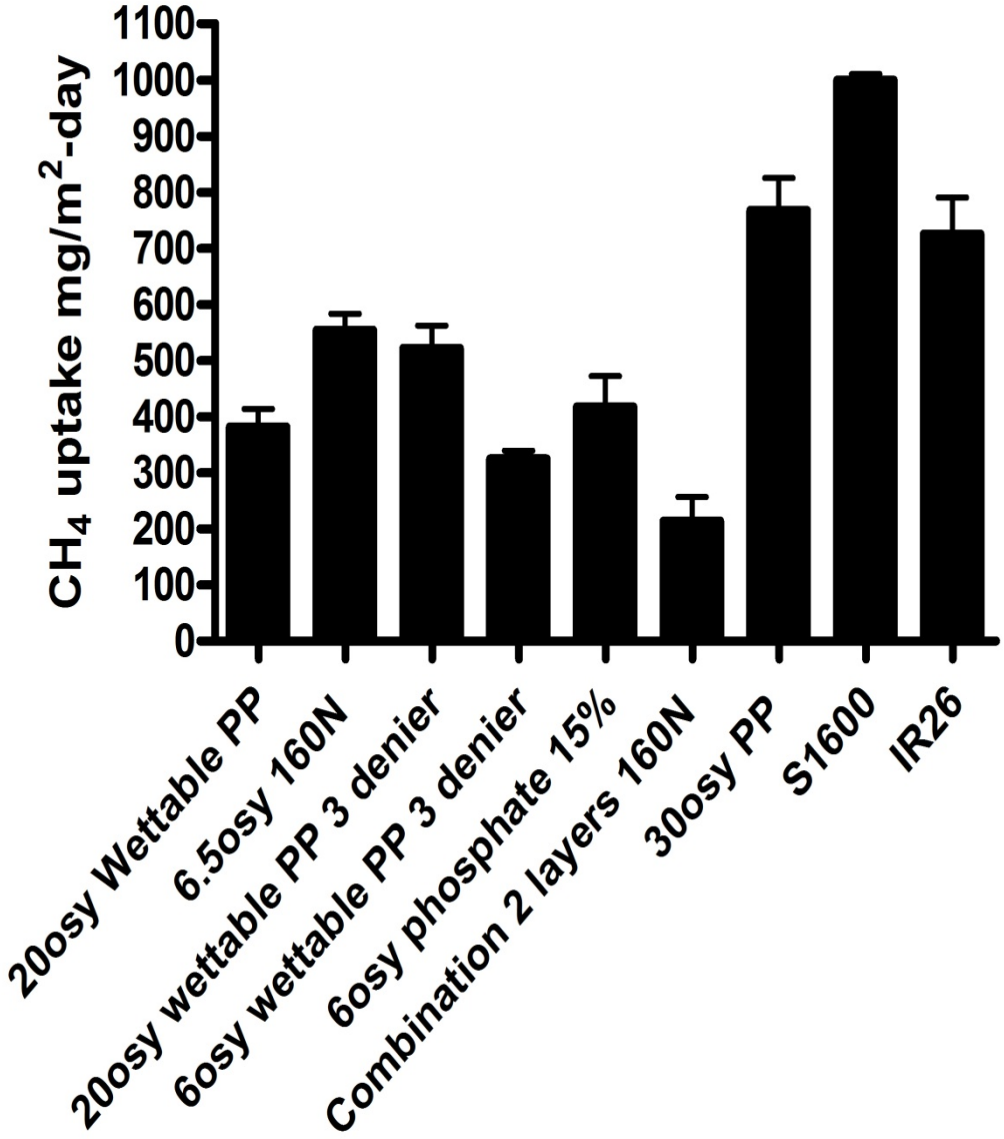
Methane uptake

- 3 geotextiles supported in excess of **700 mg CH_4** uptake/m^2/day : **G, H, I**

- **Statistically significant differences between** 30 osy PP, S1600 and IR26 compared to all other samples (one-way Anova, $p<0.05$).

- In general, these three were **among the thickest matrices**.

- On the other hand, **thickness was not the sole influential factor** because 20 osy wettable pp did not show high methane oxidation activity

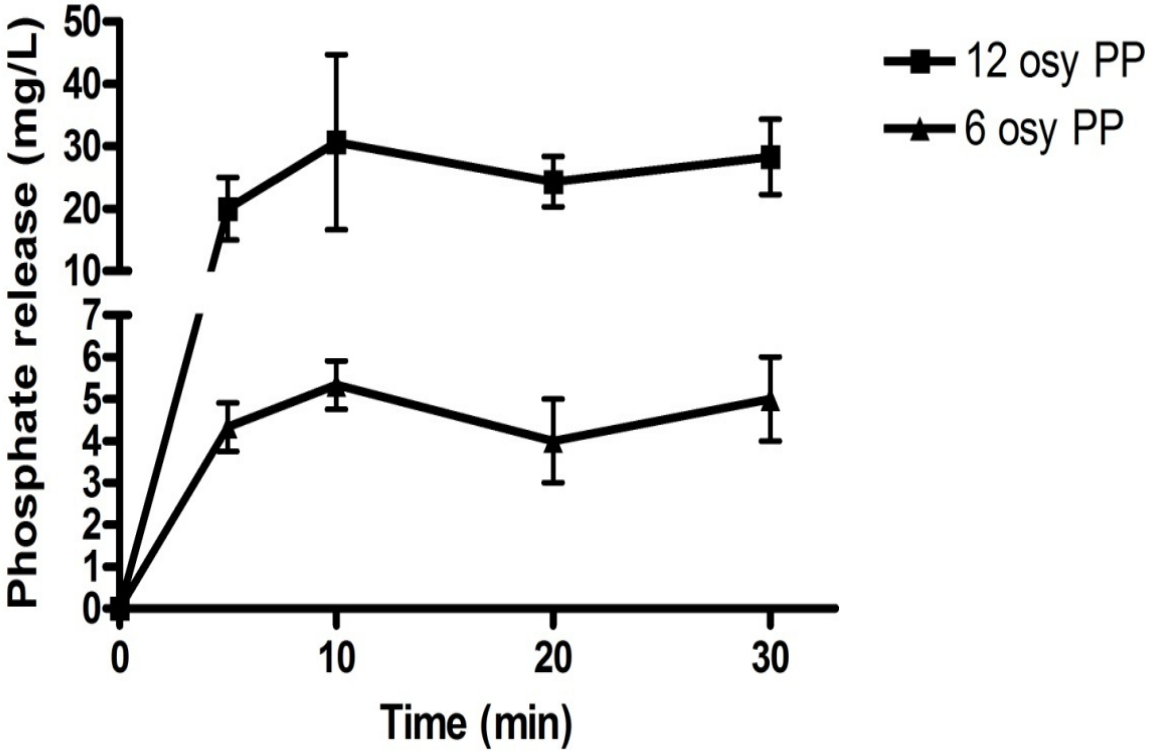


Phosphorus release

- Some geotextiles impregnated with **phosphate by the manufacturer (as a fire retardant)** were included among the candidate materials tested. It was thought that the additional **nutrient might enhance methanotroph growth**.

- The materials were tested for their propensity to release orthophosphate (PO_4^{-3}) when wetted. The results indicated that there was **very high phosphate release** within the **first 5 min of contact** with DI water.

- It was judged that such rapid release could cause **osmotic stress** for the methanotrophic bacteria, and use of these tarp candidates was discontinued.



Tarp Selection

- When drained, **I had the highest water holding capacity. A and H both held over 90% as much as I.**
- When wrung dry, H had the highest capacity, followed by tarp I (88%) and tarp A (82%).
- **H would be a full kg lighter than I per m^2 (3 vs 4 kg)**.
- Tarps **A, H, and I** appeared to be the most promising tarp candidates.

Percentage of Water Holding Capacity: tarp drained	Corresponding tarp	Percentage of Water Holding Capacity: tarp wrung dry	Corresponding tarp	Wring out tarp weight per m^2 (g/m^2)
100	I	100	H	2999
99.3	A	88	I	3976
92.5	H	82	A	4027
70.7	D	57	G	4245
65.5	F	46	D	1082
64.6	G	44	F	1831
56.4	E	39	B	785
37.1	C	31	E	796
29.3	D	15	C	1426

ranked according to their water holding ability relative to the **tarp with the highest water holding capacity**

Tarp Selection

- Tarps H ,I, A and G were among the most interesting. However **H and I were both thinner** and significantly better at supporting methane oxidation than tarp A.

- **Tarp G** (30 osy PP) did support methane oxidation as well as tarp I but its **water holding capacity was not as good.**

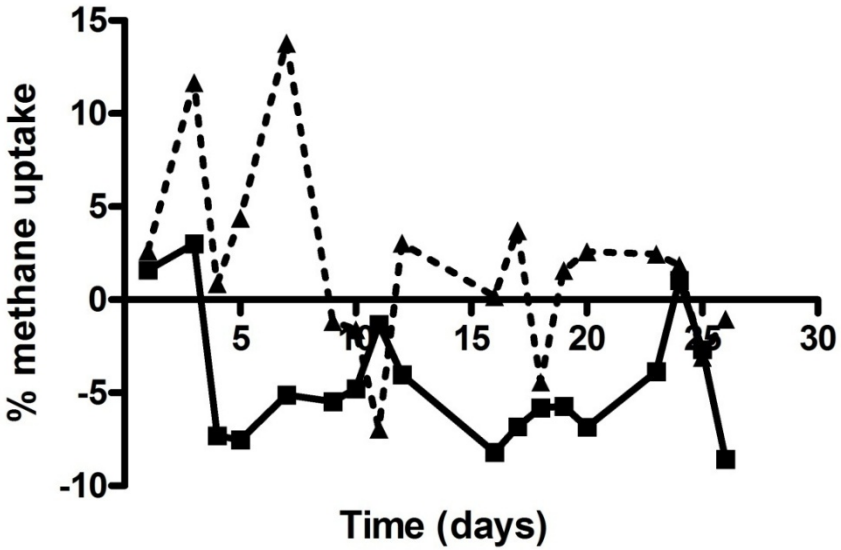
- Moreover, **S1600 (H) and IR 26 (I)** are existing commercial Ten Cate products, while 30 osy PP is from the TenCate Geosynthetics pilot plant. Since S1600 and IR26 were available in **20 ft wide rolls**, **30 osy PP** (G) was only going to be available for testing in **small quantities**.

- Also, geotextile **I, IR 26, has a fused side**, which was considered a potentially valuable characteristic. A greater resistance from the fused surface might result in a **longer retention time** in the tarp.

- **Tarp H (S1600) and I (IR26) were chosen for the continuous flow experiments**

Single layer geotextile (S1600)

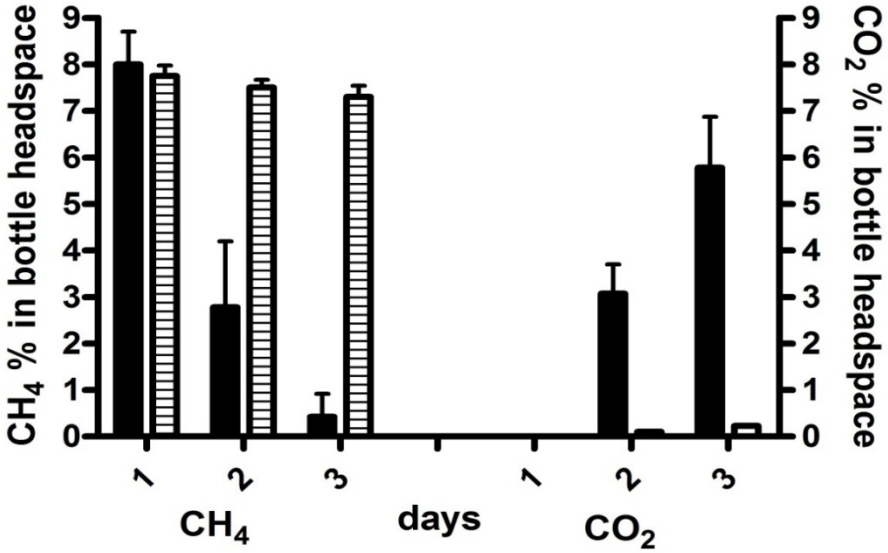
- **The biotarp** (dotted line) showed **greater activity than the control tarp** (black line).
- The maximum methane uptake by the biotarp was about 14%, but that level of **performance only lasted for about 2 d**.
- The more typical uptake rate was 0-5%. Further, there was **no detectable level of carbon dioxide in the exit gas**.



- Small pieces of the incubated tarp were **tested in batch for methane uptake.**
- Activity by the biotarp (black) but not by the control (striped) suggests:

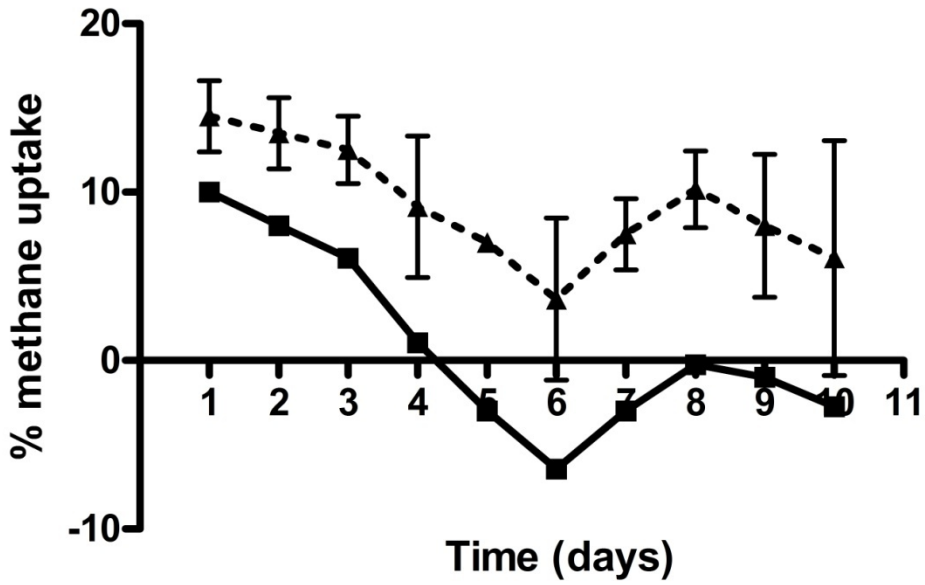
(i) the methanotrophic bacteria embedded in the tarp were **still oxidizing methane**.

(ii) the continuous flow **chamber configuration did not reveal such activity**.



Dual-layered Geotextiles

- **A composite tarp** containing one layer of **IR26** and one layer of **S1600** was created.
- Results from the **dual layer biotarp were better** than those observed for the single layer tarp.
- Biotarp peak methane uptake was **about 14%**, and the consumption was more **regular**.

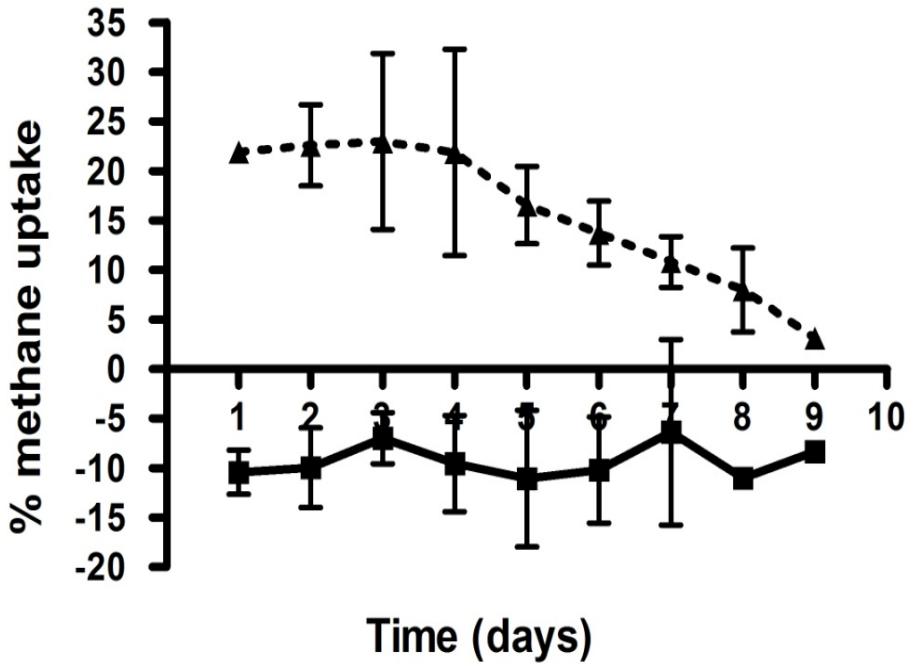


- Unlike the single-layer tarp experiments, there was **evidence of water vapor production**.
- Unfortunately, the control tarp (black line) also showed methane uptake activity, suggesting that the **readings were not accurate** or that there was biotic activity in the control. Since batch tests in Experiment 1 showed the control was inactive, the differences between the active and control tarp are likely real, but the measurement techniques must be improved.

Multilayer geotextile

- **IR26 and S1600 geotextiles were layered alternately,** with an IR26 piece in the second and fourth (top) layer placed **fused side up.**

- The four-layered biotarps (dotted line) had an **average methane uptake rate of 24%, with a peak rate of 35%.** The highest rate was maintained for 4 d then **decreased steadily down to** 3% uptake on Day 9.



- **Condensation** was evident on the walls of chambers containing biotarps (dotted line), but not on the walls of the controls (black line). Moreover **production of carbon dioxide** was observed (4 -18 % of the exit flow).

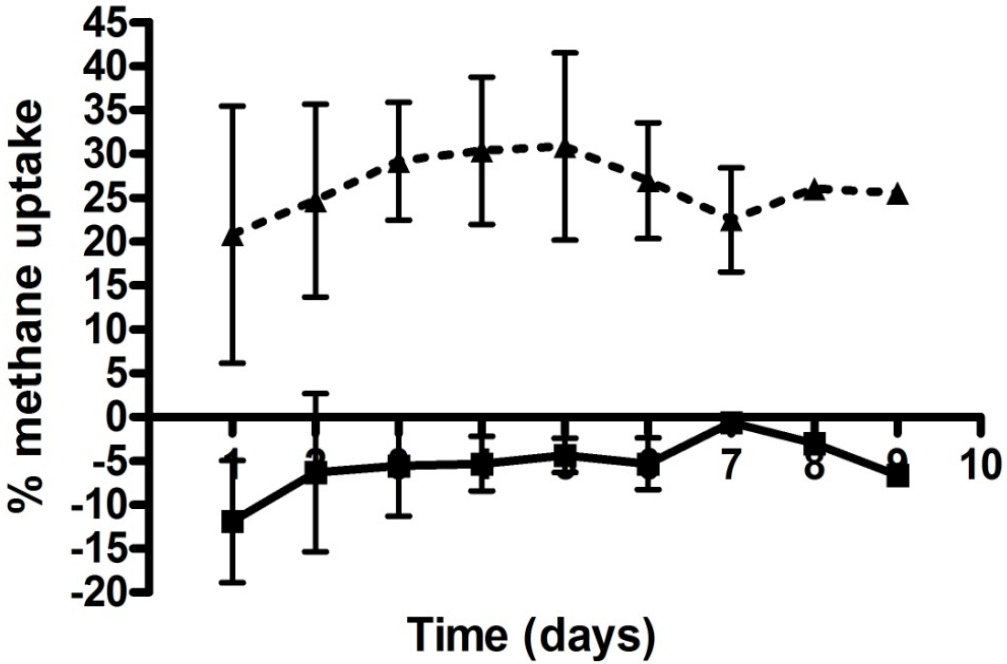
- The control was steady but still had a **negative uptake.**

Multilayer with soil

- A thin layer of **landfill cover soil** was added to the composite tarp (between the second and third layers) to determine whether or not it **could enhance the biotarp methane uptake rate.**

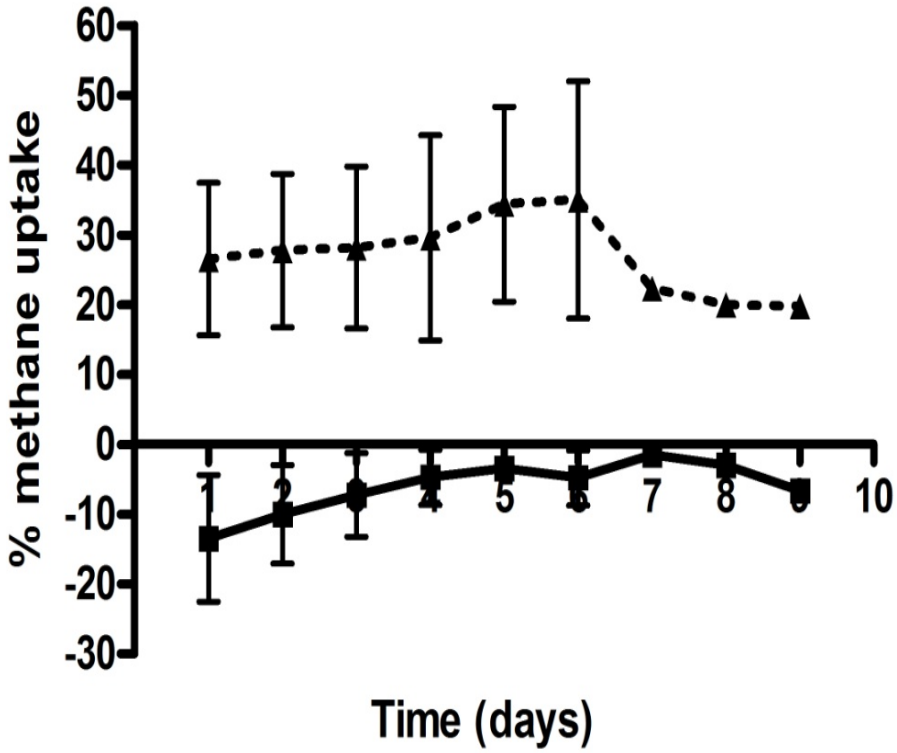
- 400 g of soil were **incubated in** a gas-tight jar **under a 50% methane** in air headspace **for 2 d**.

- One sample reached **a peak of 41% methane uptake**. **An average uptake rate of 30% was** observed throughout the 9 d of testing.



- **Condensation accumulated** on the walls of the continuous flow chambers, and **carbon dioxide production** was robust (ranging from 7 to 22% of the exit flow).

Multilayer with compost



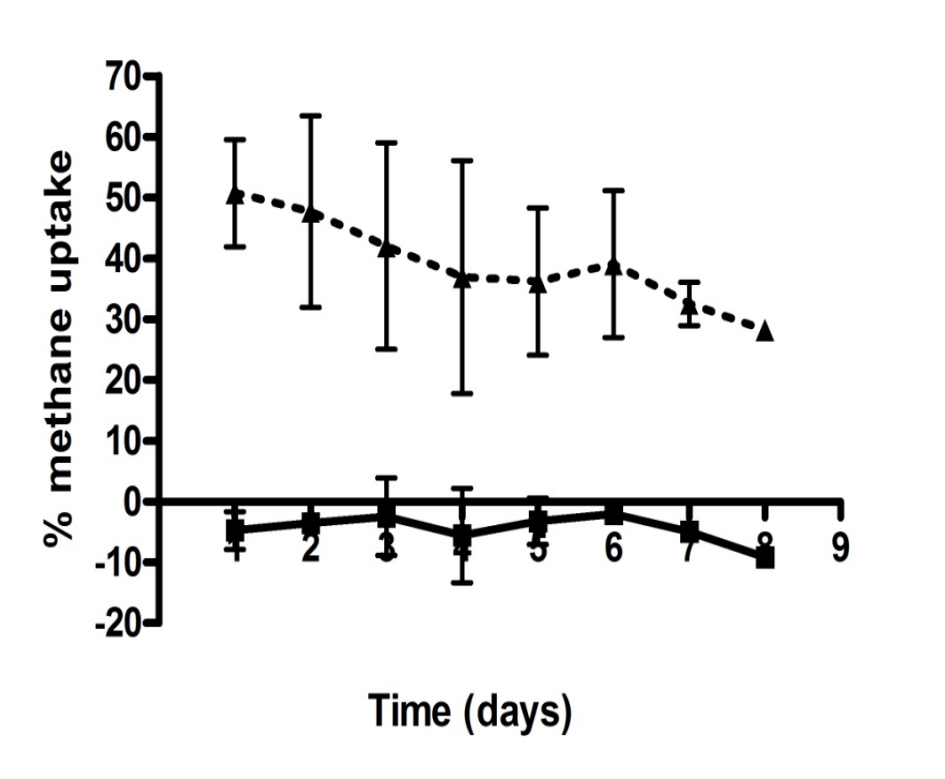
- Compost has been shown to be a **good host matrix for methanotrophs like in Biofilters.**

- Like the soil, the compost was **pre-incubated** in a gas-tight jar with a 50% methane-in-air headspace for two days.

- **The mean methane uptake rate was 31%**, although the **variability** between replicates was very high. One biotarp reached **a peak rate of 51%.** Overall, the methane uptake rate was in the range of 20% over the nine days of incubation.

- **Water condensation** and **carbon dioxide production** were evident. The carbon dioxide concentration ranged from 11 to 55% of the exit flow.

Multilayer Biotarp with Shale



- Shale is a very small and light rock often used in aggregate to lighten concrete. It is **extremely porous** and has been shown to be an effective **methanotroph support in methane biofilters**.
- Prior to the experiment, **the shale was bathed** either in a liquid culture of methanotrophs or in sterile NMS for about 30 min.
- The **methane uptake averaged about 50% initially** and fell to about **30%** at the end of 8 d.

- One biotarp showed a peak methane uptake rate **of 62%.**
- As with the other trials, there was **water condensation** on the chamber walls, and the **production of carbon dioxide** here was the highest for all trials (ranging from 15 to 38%).

Continuous Flow Chamber Results Summary

- The **odd control results** were likely due to the fact that **even slight airflow changes in airflow in the room greatly influenced the flow readings**. By the end of the experimental period, all tests were conducted with the laboratory door closed and with a three-sided Plexiglas shield installed in front of the reactors.
- Increasing the number of geomembrane layers increased methane uptake. **Additional layers provided more retention time.**
- **Amendments such as soil, compost and shale**, appeared to **stabilize the long term performance** of the methanotrophs. Their contribution may have been due to:
  - **Additional methanotrophs** (Soil and compost pre-incubated)
  - **The porous nature of the shale increasing methanotroph density**
  - **Supplementary nutrient addition** (soil and compost)
  - **Additional water holding capacity** (compost)

Pilot Field Tests

- Using a mechanical auger, six holes were dug through the intermediate cover to reach the **one year old buried refuse.**
- Between **mid-November and mid-December 2007** (ambient air temperature 6-24°C), six measurements were made at each chamber site.
- The flux atop the bare refuse was high, with the mean values for each chamber ranging from **432-5337 g/m^{2}-d.**
- The highly variable mean rates were collected from chambers **within a 20 ft by 20 ft square area.**
- For a given chamber, the flux readings were also **very variable**, with coefficients of variation ranging from 12-36%.

Fluxes Directly Atop Solid Waste

	Average Methane Flux (g/m^{2}-day)	Standard Deviation
Chamber 1	1092	167
Chamber 2	2527	451
Chamber 3	5337	640
Chamber 4	2576	926
Chamber 5	4161	546
Chamber 6	432.0	110

Pilot Field Tests

- An open cell flux is more likely to be in the range of **100-200 g/m^2-d**.
- Chambers were set directly on the **surface of the cover.**
- Flux measurements were repeated from **mid-January to mid-February 2008** (ambient air temperature 2°-13°C).
- Fluxes through the intermediate cover were quite **low and extremely variable** between chambers and within replicate chamber readings taken on different days.
- Fluxes **above 30 g/m^2-d were rarely measured**

	Average Methane Flux (g/m^2-day)	Standard Deviation
Chamber 1	8.55	6.9
Chamber 2	31.1	24
Chamber 3	6.39	5.5
Chamber 4	32.9	38
Chamber 5	12.1	8.5
Chamber 6	9.46	13

Pilot Field Tests

- Recessing the flux chamber bases **about 8 in into the intermediate cover** yielded a good range of bare soil fluxes.

- The average methane flux **from June to August 2008** for the six chambers were judged to be in a good representative range of fluxes.

- However, for a given chamber and between the chambers, the fluxes were still very **variable** day to day. This was likely due to temperature, atmospheric pressure and precipitation.

	Average Methane Flux (g/m^2-day)	Standard Deviation
Chamber 1	51.57	49.9
Chamber 2	128.4	101
Chamber 3	139.4	104
Chamber 4	27.15	55.1
Chamber 5	5.230	1.91
Chamber 6	175.8	90.8

Concluding Remarks about Landfill Test Protocol

- The **high variability** in day-to-day flux readings made it **difficult to judge** whether or not certain sites would **reliably** emit fluxes in a range that would be useful for biotarp testing.

- The final resolution requiring the chamber bases to be recessed in the ground generated **new problems with rainwater accumulation.**

- The pretests yielded reliable methods for sample collection and flux calculations and revealed some of the challenges that will be encountered in field testing.

- **Field tests will challenge the biotarp prototypes** with intermittent starvation, changing temperatures, rain events, and varying methane emission rates.

Conclusions

- The **water holding capacity** and the ability of a specific geotextile to support good **methane oxidation** were the main characteristics used to choose geotextiles suitable for testing in the continuous flow chamber. **Two geotextiles**, **IR26 and S1600,** were the focus of continuous flow chamber tests.

- The chamber experiments quickly revealed that **retention time** is an important factor for biotarp success. Tarps showing undetectable methane uptake levels in the chambers subsequently consumed methane in 24 h batch experiments.

- **Multilayer tarps** improved biotarp performance, but **the addition of soil, compost or shale enhanced methane oxidation** even further. This may have been due to the water holding capacity of these materials, their methanotroph **adsorption properties**, or in the case of soil, **trace elements** of microbial by-products that stimulated methanotrophic bacterial growth.

- On the field test site, repeated flux measurements atop intermediate cover, on 1-year old bared refuse and in the middle of the intermediate cover showed **high variability day to day**.

Recommendations

- Continue to explore **alternate materials** to see if a thicker but lighter material with good water holding capacity could be found. The current four-layer biotarp is likely **too thick and heavy** to be feasible.
- Biotarp support matrices that could easily **accommodate the soil or shale amendments** should be sought and tested.
- **Different ranges of methane flux** should be tested to see how a biotarp could adjust to much higher or much lower flux rates.
- **Microscopy** could be used to determine the **way in which methanotrophic bacteria populate the tarp**.
- Starvation cycles, long-term performance, resistance to the rain, **response to ammonia flux**, and response to varying moisture content should be investigated.