Development of a Technique to Quantify CH$_4$ Oxidation and Encourage Field Implementation of Biocovers

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TAG Meeting 1
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TAG Meeting 1: Agenda

• Call meeting to order (Abichou)
• Introductions
• Overview of Project Scope and Objectives (Abichou)
• Research Tasks (Abichou)
• Expected Research Outcomes (Abichou)
• Discussions (Group)
• Field demonstration of Gas Push Pull Test (GPPT)
  (Outside the College of Engineering)
Previous Research on Methane Oxidation by our team

Cost Effective Approach to Mitigate LFG Emissions
Background: CH₄ Oxidation

- \[ \text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \] (Biological)
- Many studies using various types of biocover materials to attenuate CH₄ emissions have been performed both at laboratory and field scale.
- The results demonstrated that CH₄ emissions can be effectively reduced using compost, amended sandy soils, to name few, as cover materials using several mechanisms.
- Methane oxidation is included in all or most inventories of greenhouse gas emissions from landfills.
- The default percent oxidation in cover soil is 10%, but through the work of our research team, the U.S. EPA has proposed a change to the 10% rule.
- One of the main issues delaying the field implementation of biocovers capable of reducing CH₄ emissions from landfills, is the lack of a proper field technique to assess the level of CH₄ oxidation under field conditions.
Background: CH₄ Oxidation, Stable Isotopes

Only specialized Stable Isotope (SI) based methods are capable of determining **percent oxidation** or **fraction oxidized** under field conditions:

- Not widely available
- Costly
- ...........

**Stable Isotope Determination of Methane Oxidation**

The addition of an extra neutron has a subtle but significant effect on chemistry

1²C = 98.9% abundant 1³C = 1.1%

The “δ” Scale

\[ \delta^{13}C_{\%} = \left( \frac{R_{\text{sam}}}{R_{\text{std}}} \right) - 1 \times 1000 \]

Where \( R = \frac{13C}{12C} \) ratio

-60% = value of methane where it is produced, before oxidation
The more + the value, the more oxidation
-50% indicates some oxidation
-40% indicates even MORE oxidation

**1²CH₄** reacts faster the **1³CH₄** leaving residual methane **1³C** enriched, or heavy

These molecules react faster

This bond is harder to break

\[ \delta^{13}C \text{ of } CH₄ = -60\% \]

**1³C tracing of Methane Oxidation**

0% -60%
25% -53%
50% -45%
75% -37%
99% -31%
100% No signal

% oxidation Isotope signal

OXIC Zone

Bottom Flux

Anoxic Zone
Rationale

- Finding possible alternatives to replace the Stable Isotopes technique to field-assess methane oxidation and to field-estimate CH$_4$ oxidation capacity of different cover materials and different cover designs is beneficial.
- One of the best possible techniques is the Gas Push Pull Test (GPPT).
- To date, the GPPT method has been used to determine rates of methane oxidation above a contaminated aquifer, in a peat bog, and only TWICE in landfill cover soils.
- We believe we have the capability to modify the GPPT and adopt it to replace and/or improve the Stable Isotope technique.
Gas Push Pull Test (GPPT)

Concept...Simple

- Push gas in, let bacteria and soil react with it, pull it back up
- Compare what you push in to what you pull out and you can assess reaction rates
Difference between the Tracer and the Reactive Gas curves are used to estimate reaction rates. This makes this measurement of oxidation more STRAIGHT FORWARD to explain.
GPPT and Reaction Rates

- Particularly useful in determining rates of chemical and microbial reactions
- Reactions are detected and quantified by the decrease in dilution-adjusted concentrations or by the increase in concentration of a reaction product
- Advection, dispersion, diffusion, sorption, mass transfer, etc… will also affect the measured tracer concentrations.
- The effects on the tracer are accounted for in various ways depending on the type of test
GPPT and Reaction Rates

• Two simplified methods:
  – Snodgrass and Kitanidis 1998: Zero-order reaction rates
  – No need for soil physical properties
Determination of Reaction Parameter
(Example: zero order)

Reaction Rate
Constant

Elapsed Time, min
Our Experience with GPPT:

We came along way with the design and the specifics of the test. We developed the technique for $\text{H}_2\text{S}$ reactivity with cover soils.

55 Gallon Drum Tests

Sand Box (7’ x 7”) Tests

We were able to run GPPT using battery powered pumping system: This will make GPPT use in field less challenging by eliminating the need for a generator.

Landfill Cover Field Tests
Our Experience with GPPT:

• Experimentally compared transport of the reactant gas and tracer gases during GPPTs as a function of varying injection/extraction flow rates in a porous medium and in the absence of microbial activity.

• Experimentally compared transport of the reactant gas CH$_4$ and tracer gases during GPPTs as a function of varying injection/extraction flow rates in a porous medium with presence of microbial activity.

• GPPTs were performed at different gas flow rates and different water saturations in a large sand-filled test pits.

• GPPTs were performed at actual landfills in Florida and will continue next year.
Our Experience with GPPT:

- We eliminated the need for TRACER GAS to be of similar molecular weight to REACTIVE GAS
- Users can correct for a Tracer with different molecular weight than their Reactive gas

This can result to wider use
GPPT in clean fine sand

- Previous research have shown that H$_2$S does not react with sand
- However, difference in breakthrough curves is measured in GPPT performed with H$_2$S in clean sand
- The difference in breakthrough curves must be due to difference in MW (134 VS 34)
GPPT in clean fine sand

- Using our developed corrections
- Corrected breakthrough curves represent a breakthrough curve of tracer with MW of 34
- The corrected results show little to no reaction of $\text{H}_2\text{S}$ with sand
GPPT of H$_2$S in clayey soils with absence of biological activities: Need to separate reactions with soil minerals from other slower reactions

Typical Breakthrough Curves

Reaction occurs too fast for GPPT to capture

Need to separate rate of early instantaneous reactions between soil minerals from the other slower reactions
GPPT of H$_2$S in clayey soils:

- We were able to separate early instantaneous reactions between soil minerals from the other slower reactions.
- The corrected results show little or no reaction of H$_2$S with iron rich clayey soil because no biological activities exist in the clayey soil.
GPPT of H$_2$S in clayey soils with presence of biological activities: Need to separate reactions with soil minerals from other slower reactions.

We were able to separate the two reactions and quantified both rates.
GPPT in Landfill Cover Soils

- Using our developed corrections
- Corrected breakthrough curves represent a breakthrough curve of tracer with MW of 34
- The corrected results show reaction of H$_2$S with landfill cover soils.
What’s Next: Shifting to Methane Oxidation

- Perform and adjust GPPT tests to field conditions and perform a field-scale tests at the Leon County Landfill and the Spring Hill Landfill
- Develop a set of guidelines to use GPPTs to quantify H$_2$S attenuation and methane oxidation in the cover-soil
- Develop a test standard on how to use the GPPT in landfill soil cover.
Motivation and Objectives

• We propose to continue GPPT methane oxidation and continue testing the method through a series of lab studies and then apply it in the field.
• We believe we have a chance to contribute to this area of research.
• We believe we will be the first team to tackle such a complex problem.
Where to go from here

- Perform and adjust GPPT tests to field conditions and perform a field-scale tests at the Leon County Landfill and the Spring Hill Landfill
- Have been invited to perform GPPT in two Indiana landfills
- Have been invited to perform GPPT in one Oregon Landfill
- Develop guidelines to use GPPTs to quantify kinetics of methane oxidation in the cover-soil Perform a field-scale tests and develop guidelines to use GPPTs to quantify kinetics of methane oxidation.
- Develop a test standard and a video on how to use the GPPT in the field to assess methane oxidation in Biofilters, Biocovers, and any landfill soil cover.
Our Experience with GPPT:

We have a graduate and an undergraduate students with extensive GPPT experience.
Expected Benefits

To help the decision-making process for future full-scale implementation of control of low-level methane emissions using engineered bio-based systems.

The engineering challenge for the design is to quantify their performance in the field and to monitor their long term efficiency.

The challenge is to obtain a long term performance equivalent to that of a thermal system.

The development of an alternative technique to field assess methane oxidation in the field will be very beneficial for field implementation engineered bio-based systems.
Expected Benefits:

Training of future researchers
Thank You

QUESTIONS