Modeling and Control of Gas Ebullition in Capped Sediments

Priscilla Viana, Ke Yin, Xiuhong Zhao, and Karl Rockne (krockne@uic.edu)
(University of Illinois at Chicago, IL USA)

ABSTRACT: A major concern in sediment capping effectiveness is gas ebullition from organic matter biodegradation in sediments. Gases may open advective channels that can result in substantial pollution release. The aim of this study was to determine the gas ebullition rate in sediments in preparation for construction of an active capping technology demonstration at the Collateral Channel site in the Chicago River. Sediment samples were collected from five sites along a transection of Collateral Channel from the combined sewer outfall at the Channel terminus. Biogenic gas production was measured in samples incubated at 5° to 35° C. Gas production followed a first order reaction trend and Arrhenius plots were obtained to determine the temperature dependence of the kinetic rate. These allowed us to predict gas ebullition for the annual temperature variation in the sediments. CO₂/CH₄ ratios change with temperature, with lower ratios at lower temperatures suggesting dominance by acetoclastic methanogens. These data were used to select adequate active capping remedial alternatives for the Channel. We conclude that wide variations in gas production occur, necessitating gas capture/control during the elevated temperatures of summer. To achieve this, an innovative geo-mesh material with an overlying highly permeable layer will be employed.

INTRODUCTION

Gas ebullition due to methanogenic activity in sediment caps has yet to be fully investigated; even though it is known that methanogenic organic matter degradation facilitates contaminant transport through caps and gas accumulation may cause cap damage (Reible, 2005). Gas bubbles generated due to methanogenic activity are hydrophobic and tend to accumulate hydrophobic contaminants and colloids on their surface. If the amount of gas produced is too high, the gas will evolve in a separate phase and the cap may burst, particularly in unconsolidated surface layers. The aim of this study is to estimate the amount of gas that may be produced at Collateral Channel (Chicago, IL, USA) on an annual basis and to evaluate the methanogenic activity due to acetoclasts and hydrogenotrophs in the surface grab samples.

Collateral Channel is a former navigation slip to the Chicago Sanitary Ship Canal (CSSC) located near Kedzie Avenue, Chicago, IL, USA. A large combined sewer overflow (CSO) is located at the head of the Channel. The CSSC is dominated by industrial and commercial land uses. However, there are plans for urban ecological restoration in the area. Through many decades contaminants were deposited in Collateral Channel with polycyclic aromatic hydrocarbon (PAH) concentrations approaching 1500 mg/kg and lead concentrations up to 228 mg/kg (see companion paper by Zhao et al., 2007).

Methane and carbon dioxide are end products of the degradation of organic matter under anaerobic conditions. In the complex process of organic matter degradation, fermenters degrade the more complex organic matter producing monosaccharides, fatty acids/alcohols and hydrogen. Under low hydrogen concentrations, syntrophic bacteria
consume those fatty acids and alcohols producing acetate, carbon dioxide and hydrogen that may be consumed by homoacetogens to produce acetate, and also by hydrogenotrophs to produce methane. Additionally, homoacetogens degrade monosaccharides producing acetate, which can then be converted to methane and carbon dioxide by acetoclastic methanogens (Conrad, 1999). The microbial community structure (and thus the volume and type of gas produced) is strongly affected by temperature changes. Hydrogenotrophic methanogens are stimulated by increased temperature to a greater extent than are acetoclastic methanogens (Conrad et al., 1987). Hydrogenotrophs produce only methane, consuming carbon dioxide and hydrogen, while acetoclasts produce methane and carbon dioxide as shown in equations 1 and 2.

Hydrogenotrophic methanogenesis

\[ CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad \Delta G_0 = -131 \text{ kJ/mol} \]  \hfill (1)

Acetoclastic methanogenesis

\[ CH_3COO^- + H^+ \rightarrow CH_4 + CO_2 \quad \Delta G_0 = -76 \text{ kJ/mol} \]  \hfill (2)

**MATERIALS AND METHODS**

**Sampling.** Surface grab samples were collected along the east transect of Collateral Channel as described in Zhao et al. (2007) (Figure 1). Surface grab samples were chosen to represent the likely “worst case” scenario with the most diagnostically young organic matter in the surface layers and thus the highest gas production potential.

**Physical/Chemical Analyses.** Organic carbon content was determined by elemental analysis (FlashEA® 1112, Thermo Electron), nitrate and sulfate were determined by ion chromatography (Dionex IC25), organic matter content and percent solids were determined as described in Zhao et al. (2007). The samples from sites five to nine (see Figure 1) were homogenized and a 100 mL subsample was added to serum bottles, sparged with nitrogen gas, sealed and incubated upside down quiescently at 5°C, 20°C, 25°C or 35°C. Volumetric gas production was monitored with a calibrated syringe in duplicates and killed controls. Methane and carbon dioxide were quantified by gas chromatography with thermal conductivity detection (9300B, SRI instruments).
RESULTS AND DISCUSSION

The results for nitrate and sulfate concentration in pore water can be observed in Figure 2A. The amount of nitrate was very low, but there was some sulfate present. Considering the immediate commencement of gas production, the very high ratio of methane production to carbon dioxide observed since the beginning of the incubation period and the total amount of methane produced during a one year period, it is clear that sulfate was rapidly consumed and methanogenesis was the predominant microbial activity at these sites. The organic matter content of the samples (Figure 2B) was as high as 32%, while the solids content varied from 10 to 26%. Consumption of all sulfate at site 8 would at most account for oxidation of 34 mmol C/L, a small fraction (<1%) of the total organic carbon in the sediment.

Gas production varied substantially as a function of temperature and site location (Figures 3 and 4). The highest amount of gas production was observed at site 5 nearest the CSO (Figure 4). Gas production decreased as the distance from the CSO increased. We speculate that less diagenetically aged organic matter near the CSO probably stimulated these higher rates of gas generation. Summer temperatures result in three times more gas production than winter temperatures.

The biogenic gas production reaction rate constant \( k \) was calculated for each site using the Fujimoto method (Figure 5) assuming a first order depletion of available methanogenic substrate as shown in equation 3. It can be observed that the rate constant values decrease as the distance from the CSO increases, showing the impact of the wastewater and storm water discharges in the past. Rate constants were plotted on an inverse temperature Arrhenius plot to obtain the activation energy for methanogenesis \( (E_a) \). The mean activation energy of methanogenesis for all sediments was 43 ± 17 kJ/mol (Figure 6). Site 5 (near the CSO) had material that was more biodegradable, while site 7 likely had a more complex substrate, as shown by its higher activation energy.

\[
C(t) = C_{\text{max}} (1 - e^{-kt})
\]  

(3)
Our results agree with methanogenic $E_a$ values reported in the literature (Table 1). Values ranged from 27 – 138 kJ/mol; the lowest observed with simple substrates (phenol) and higher values were observed with more complex organic compounds like fulvic acids and humic acids commonly found in peat soil.

The volume of gas that may be produced at each site per cubic meter of sediment was estimated for the whole year (Figure 7). Gas production at site 5 (nearest the CSO) may exceed 4 m$^3$ gas/m$^3$ sediment. Sites 6, 7 and 8 all exceed 2 m$^3$ gas/m$^3$ sediment. Site 9, most distant from the CSO, was the only site containing sediment that would not produce gas in excess of its own volume on an annual basis. Although these sediments were disturbed during experimental set up (and therefore may represent a higher value than in undisturbed sediments in situ) we argue that it still may represent a realistic prediction under capping scenarios because the sediment will be disturbed during cap placement.
TABLE 1. Activation energy values from literature.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>$E_a$ (kJ/mol)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wetlands (fen soil)</td>
<td>138±17 (unsaturated)</td>
<td>(Prieme 1994)</td>
</tr>
<tr>
<td></td>
<td>84±6 (saturated)</td>
<td></td>
</tr>
<tr>
<td>Wetlands</td>
<td>74.3 – 79.5</td>
<td>(MacDonald et al. 1998)</td>
</tr>
<tr>
<td>Wetlands</td>
<td>29 – 50 at 51 d</td>
<td>(Westermann 1993)</td>
</tr>
<tr>
<td>Primary sludge</td>
<td>50</td>
<td>(Mahmoud et al. 2004)</td>
</tr>
<tr>
<td>UASB reactor (phenol)</td>
<td>27.2</td>
<td>(Chou et al. 2004)</td>
</tr>
<tr>
<td>Paddy soil</td>
<td>59.7</td>
<td>(Cai and Yan. 1999)</td>
</tr>
<tr>
<td>Paddy soil</td>
<td>91.0</td>
<td>(Conrad et al. 1987)</td>
</tr>
<tr>
<td>Wetland rice soil</td>
<td>48 - 65</td>
<td>(Yao and Conrad 2000)</td>
</tr>
<tr>
<td>120 mL serum bottles (45 mL mineral</td>
<td>121±1</td>
<td>(Chin et al. 1999)</td>
</tr>
<tr>
<td>medium, 2 mL amorphous cellulose)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peat soil</td>
<td>123 - 271</td>
<td>(Dunfield et al. 1993)</td>
</tr>
<tr>
<td>Alder swamp</td>
<td>92 - 110</td>
<td>(Westermann and Ahring 1987)</td>
</tr>
<tr>
<td>Lake sediment</td>
<td>76</td>
<td>(Thebrath et al. 1993)</td>
</tr>
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The maximum amount of methanogenic substrate ($C_{max}$) was estimated for each sediment from the first order depletion kinetic model (Equation 3). Comparing the total organic carbon content value at each site (Figure 8A) with the $C_{max}$ value (Figure 8B) indicates that the amount of substrate available to methanogenesis is very low. Well less than 10% of the total organic carbon could be accounted for as methanogenic substrate, even after more than a year of incubation. It is likely that the organic matter that could serve as methanogenic substrate was depleted, leaving behind more complex organic matter.

The ${\text{CH}_4}/\text{CO}_2$ ratio of biogenic gas was affected by temperature (Figure 9). Lower ratios were observed at lower temperatures, suggesting dominance by acetoclastic methanogens. Higher gas production and higher ${\text{CH}_4}/\text{CO}_2$ ratios were observed at sites 5 and 6 at low temperatures than for the other sites, suggesting a greater prevalence of hydrogenotrophic methanogens.
FIGURE 8. (A) Organic carbon content of surfacial Collateral Channel sediments as a function of distance from the CSO and (B) $C_{\text{max}}$ at each site as a function of

SUMMARY AND CONCLUSIONS

Due to the high amount of gas produced, particularly at site 5, gas control will likely be needed for this site to ensure cap integrity. To achieve this, the design team will employ a geonet layer with overlying high permeability sand between the contaminated sediment and the cap material to collect the gas at the sides of the Channel. This will prevent the cap from potential breach by gas ebullition. Monitoring of gas production for an entire year was important to better predict the amount of gas produced. This can be seen by comparing the predicted gas ebullition from a short term (30 d) data set. Gas production would be overestimated by a factor of 2–3. The activation energy of methanogenesis in Collateral Channel sediments is 43.4 ± 17.0 kJ/mol. The amount of organic carbon available as substrate for methanogenic activity is very low, suggesting that sedimentary organic carbon is a poor predictor of methanogenic activity.

ACKNOWLEDGMENT

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REFERENCES


