

Methanogenic biodegradation of charcoal production wastes in groundwater at Kingsford, Michigan, USA

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Abstract A house exploded in the City of Kingsford, Michigan USA. The explosion was caused by CH₄ that leaked into the basement from the surrounding soil. Evidence suggests that biodegradation of products from the distillation and spillage at or near a former wood carbonization plant site was the major source of CH₄ and CO₂ in the groundwater system. The plant area is directly upgradient from deep groundwater, samples of which are green-yellow in colour, have a very strong odour of burnt wood, contain high concentrations of mononuclear aromatic and phenolic compounds, and extremely high concentrations of volatile fatty acids. The majority of the dissolved compounds in these groundwater samples have been shown, using laboratory microcosms, to be anaerobically biodegradable to CH₄ and CO₂. The biodegradable compounds, and the amounts of CH₄ and CO₂ produced in the microcosms, are consistent with observations from field samples.

Key words biodegradation; charcoal; contamination; groundwater; methane; wood distillation

INTRODUCTION

On 12 July 1995, an explosion occurred at 2104 West Breen Street in the City of Kingsford, Michigan, USA (Fig. 1). The explosion was apparently caused by methane gas that seeped into the basement from the surrounding subsurface. Subsequent studies by the US Geological Survey, US Environmental Protection Agency, the local power company, and consulting engineers determined that the CH₄ in the residence resulted from high concentrations of this compound in the soil gas. The occurrence of CH₄ was localized around this residence and subsequently a soil gas vapour extraction system was installed that lowered the high CH₄ concentrations. Studies of the stable isotopic ratios of carbon ($\delta^{13}\text{C}$ of CH₄ and δD CH₄) in water samples collected by the US Geological Survey determined that the gas was biogenic in origin, mostly from the fermentation of acetate (Michel *et al.*, 2001), and recent in age.

Wastes characteristic of a former charcoal production plant are prevalent throughout the area northeast of the house. The plant was in operation for 37 years before it closed in 1961. Analyses of shallow groundwater samples, especially in a northeasterly direction from the house towards former disposal pits at the plant, contained elevated concentrations of volatile and semi-volatile compounds characteristic of the water-soluble fraction of wood creosote wastes. Although these

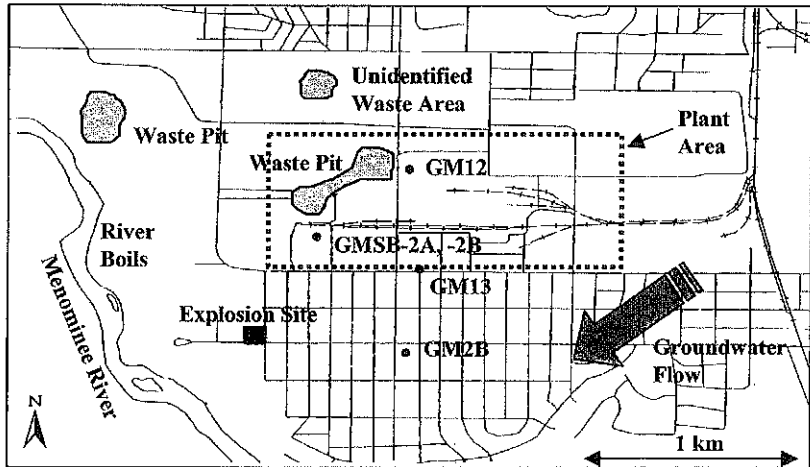


Fig. 1 Site map of the study area in Kingsford, Michigan, showing the explosion site, selected sampling sites, and the former charcoal-manufacturing site.

compounds constitute a water quality concern, concentrations of these contaminants were not high enough to account for the extremely high dissolved CH_4 ($>60 \text{ mg l}^{-1} \text{ CH}_4$) and CO_2 concentrations observed throughout the area.

A preponderance of evidence from over 750 gas and water samples suggests that discharge from waste disposal pits and leakage and/or spillage during the distillation of the pyroligneous acid (PA) fraction of the charcoal manufacturing processes, were the major sources of CH_4 and CO_2 in the deep groundwater system. The plant area is directly upgradient from the house and other seeps. Deep groundwater samples (80–90 m) in the area downgradient of the plant are green-yellow in colour, have a very strong odour of burnt wood, contain high concentrations of mononuclear aromatic and phenolic compounds ($40\text{--}60 \text{ mg l}^{-1}$) and have extremely high concentrations ($6000\text{--}7000 \text{ mg l}^{-1}$) of volatile fatty acids (VFAs). In addition, the VFAs in deep groundwater samples from three down gradient locations (GMSB-2A, GMSB-2B and GM13) have identical compound-specific isotopic ratios (Michel *et al.*, 2001).

GEOLOGICAL SETTING AND HYDROGEOLOGY

An interbedded sequence of Pleistocene-age glacial deposits forms a complex aquifer system in the Kingsford area (Westjohn & Godsy, 1997). Surficial glacial deposits consist of coarse sand and gravel; these deposits form a relatively flat topographic surface in most of the Kingsford area. These surficial glacial deposits are part of a prograded outwash terrace that formed when glacial ice occupied a position northeast of the plant site. Numerous glacial kettles form depressions on the outwash terrace surface that were used as waste disposal pits by the plant until the early 1930s. Glacial deposits that underlie outwash sand and gravel consist of laterally discontinuous beds of silt, silty clay, and clay; these deposits are interbedded with glaciofluvial sand and gravel beds, which also are laterally discontinuous. Multiple sand and gravel beds form a stacked, compartmentalized system of confined aquifers that are separated by fine-grained aeolian and lacustrine deposits. The basal part of the glacial section consists of

a carapace of basal-lodgment till, which overlies poorly permeable metamorphic rocks of Precambrian age (Michigamme Slate).

Hydraulic head in the confined part of the aquifer system near the plant site is typically 10 to 15 m lower than hydraulic head in the shallow unconfined (or partially confined) part of the aquifer system. This condition results in a steep downward hydraulic gradient, which influences the migration and transport of CH₄ and dissolved organic constituents in the glacial aquifer system. Downgradient from the plant site near the Menominee River, the hydraulic gradient is reversed to a steep upward gradient allowing the outgassing of the dissolved CH₄ at the river boils and the house explosion site.

NATURE OF WOOD CARBONIZATION PRODUCTS

From approximately 1924 until 1951, the Ford Motor Company manufactured wooden automobile parts at a plant site to the northeast of the explosion site yielding approximately 3.63×10^5 kg or 363 t (tonne) of scrap wood per day from sawmill and body plant operations (Nelson, 1930). To use this scrap, a wood carbonization and by-products distillation plant was built and several commercial products were produced (Nelson, 1930):

- **Charcoal** approximately 300 kg per tonne of wood.
- **Noncondensable gas** approximately 160 m³ of gases per tonne of wood (mostly CO₂, CO, CH₄, and N₂).
- **Wood creosote/tar** approximately 14 l creosote, 33 kg pitch, and 91 l of soluble tar per tonne of wood. These products consisted mainly of polynuclear aromatic and phenolic compounds.
- **Pyroligneous acid** approximately 460 l per tonne of wood. This fraction consists of 12.5% acetic acid, 4.5% methanol, and smaller amounts of other VFAs, solvents, and phenolic and other monoaromatic compounds.

In 1951, Kingsford Chemical Co. obtained the wood carbonization plant and continued the production of charcoal and by-product distillation until 1961.

BIODEGRADATION OF THE PYROLIGNEOUS ACID COMPOUNDS

Analytical methods for groundwater samples

The VFAs and phenolic compounds in groundwater samples were extracted by first acidifying (pH <2) and then extracting (1:1) into diethyl ether. Individual organic compounds were identified and quantified by injecting 1 µl of extract dried with CaCl₂ into a Finnigan-GCQ GC/MS. The GC/MS was equipped with a 0.25 mm ID, 30 m DB-WAXETR column with a film thickness of 0.25 µm. The injection port was maintained at 250°C in the splitless mode for 0.8 min after injection, then switched to split mode for the rest of the run. The column oven was programmed to hold at 35°C for 5 min, then increase at 10°C min⁻¹ to 240°C, and then hold for 5 min. Identifications were confirmed by comparison of the mass spectral data and retention times with known standards.

Toxicity and microbial enumeration of deep groundwater and sediment samples

Water samples from GMSB-2A did not contain culturable microorganisms (<1 cell per 0.1 ml) when tested using the methods of Godsy *et al.* (1992); however, the corresponding sediment sample contained 10^5 or greater total microorganisms per gram dry weight sediment. The lack of culturable microorganisms in this water sample strongly implies that the contaminated groundwater is hostile to microbial growth. The hostility from the high concentrations of VFAs and phenolic compounds is relieved only when there is dilution with the native groundwater during downgradient travel in the aquifer.

This finding provides a possible explanation as to why such readily biodegradable compounds have persisted for many years in the subsurface. The PA is moving vertically downward due to the hydraulic gradient and laterally with the groundwater flow. This can be seen at GM13, just south of the plant area, where the PA fraction was encountered in a grab sample taken at 44.2 m below land surface, but not in samples from the bedrock well location (99.1 m). When the PA mixes with the groundwater during downgradient travel in the higher conductivity lenses, the inhibition is relieved by dilution with groundwater, and biodegradation of the waste begins as seen in groundwater samples from GM2B.

Biodegradation of pyroligneous acid fraction in groundwater

Water samples from GMSB-2A, GMSB-2B, and GM13 are green-yellow in colour, have a very strong odour of burnt wood, contain high concentrations of mononuclear aromatic and phenolic compounds and have extremely high concentrations of VFAs. All of these ground-water samples have low dissolved CH_4 and CO_2 , a low pH, and very high TOC values. Groundwater samples from GM12 and other wells, directly upgradient from the disposal pits and the plant site, neither contains significant levels of CH_4 and CO_2 nor volatile or semi-volatile contaminants or VFAs. Samples from GM2B, approximately 425 m south of GM13, contained approximately one-fourth the concentrations of VFAs (~1000 mg l⁻¹ acetate) and phenols (1 mg l⁻¹ 3-ethylphenol), which have been partially biodegraded and diluted with ground water. Phenol and 4-methylphenol have been completely degraded during down gradient travel. The preferential disappearance indicates biodegradation rather than just dilution (Godsy *et al.*, 1992). Samples from >1000 m downgradient from the waste disposal pits and the plant site contain only trace amounts of contaminants; however, these samples contain high concentrations of dissolved CH_4 and CO_2 ,

Biodegradation of pyroligneous acid fraction in laboratory microcosms

In order to test the hypothesis that the undiluted groundwater was hostile to microorganisms and the biodegradation potential of the PA, two identical microcosms were prepared using groundwater from GMSB-2B taken at 80.1 m below land surface. Two 4-l solvent bottles were fitted with Mininert[®] valves to facilitate removal of water samples from one microcosm and gas samples from the second microcosm. Both

microcosms were prepared with 3.1 l of groundwater and 0.75 l of aged anaerobic domestic sewage sludge. The sludge performed as a methanogenic inoculum, and as a diluent to relieve the inhibition of the sample. Both were maintained in an O₂-free anaerobic glove box at 20 ± 1°C.

Microcosm analytical methods

Phenols and VFAs were determined as previously described. Gas volumes were measured using a water wetted 10-ml syringe, and gas composition, both head space and dissolved gas, was determined by head-space analysis using a GC equipped with a thermal conductivity detector (Godsy *et al.*, 1992). TOC was determined by wet-chemical oxidation (Williams, 1969).

Microcosm substrate utilization

After the microcosms were inoculated, a leak developed in the gas-sampling valve that was not detected for approximately 61 days; therefore, no samples were taken during this time. The VFAs and phenolic compounds are identified in Fig. 2(a, b) and the biodegradation during the course of the experiment in Fig. 3. Unconfirmed compounds were mainly alcohols, furans, cyclic hydrocarbons, and monoaromatic compounds. The majority of these compounds contained one or more side chains which is consistent with compounds attributed to the PA fraction (Klar, 1925).

The loss of the acetate and butyrate was readily apparent after 154 days of biodegradation, at which time the VFAs were essentially gone and the phenols were starting to biodegrade (Table 1). Low levels of acetate persisted since it is an intermediate in the biodegradation of aromatic compounds (Godsy *et al.*, 1996). Once phenol was biodegraded, 3- and 4-methylphenol were biodegraded after 253 days. After 328 days, more than 99% of the biodegradable compounds were fermented to CH₄ and CO₂. 2-Methylphenol did not biodegrade during this time, and was the last phenol to biodegrade between days 328 to 471.

After 471 days, only the nonbiodegradable 2,6- and 2,4-dimethylphenol remained. This observation was consistent with published results that find that 2-methylphenol is the most difficult and slowest of the methylphenols to biodegrade under methanogenic

Table 1 Concentrations (mg l⁻¹) of selected compounds present in water samples from the microcosm.

Component	Days:						
	0	86	124	167	192	223	328
Acetate	3196	20.8	23.9	8.7	2.7	1.3	0.2
Propionate	429	245	1.0	0.4	ND	ND	ND
Butyrate	577	345	1.5	0.6	ND	ND	ND
Phenol	8.5	8.7	8.4	ND	ND	ND	ND
3-Ethylphenol	4.3	4.4	4.1	2.7	ND	ND	ND
3- and 4-Methylphenol	25.2	26.2	23.7	27.9	27.5	3.6	ND
2-Methylphenol	4.8	4.8	5.46	3.5	3.7	3.8	4.1
2,4-Dimethylphenol	3.2	4.1	3.8	3.0	3.1	3.8	3.9

ND = not detected, generally <0.1 mg l⁻¹

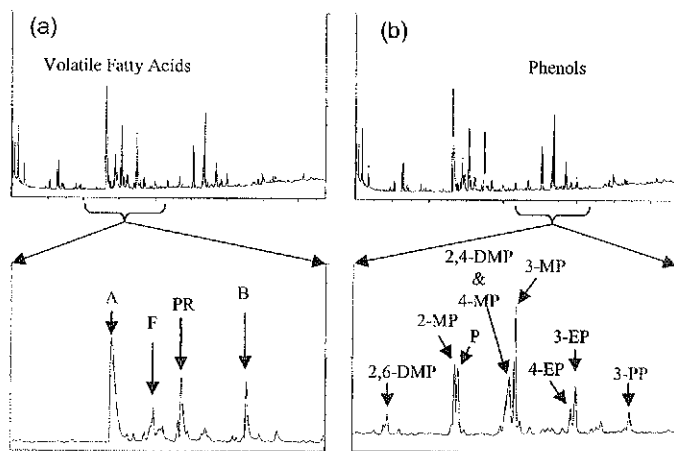


Fig. 2 Identified and confirmed VFAs (a) and phenolic (b) compounds in a groundwater sample from GMSB-2B. A = acetate, B = butyrate, F = formate, and PR = propionate, P = phenol, 2-MP = 2-methylphenol, 3-MP = 3-methylphenol, 4-MP = 4-methylphenol, 3-EP = 3-ethylphenol, 4-EP = 4-ethylphenol, 3-PP = 3-propylphenol, 2,4-DMP = 2,4-dimethylphenol, 2,6-DMP = 2,6-dimethylphenol.

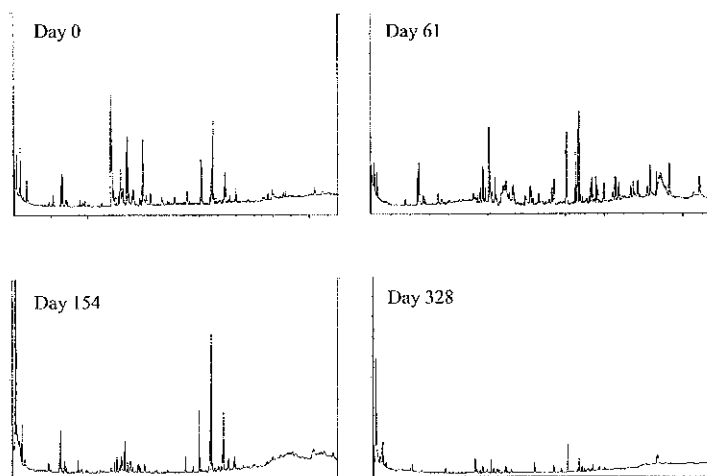


Fig. 3 Methanogenesis of the VFAs and phenolic compounds in the microcosm on days 0, 61, 154, and 328. The microcosm was prepared from a groundwater sample from GMSB-2B. The compounds are identified in Fig. 2.

conditions (Godsy *et al.*, 1992), and phenols with only one attached alkyl chain (e.g. methylphenols and ethylphenols) are biodegradable under these conditions, while phenols with two or more alkyl chains (e.g. dimethylphenols) have not been shown to be biodegradable under methanogenic conditions (Godsy *et al.*, 1992).

Mass balance

A mass balance of carbon transformation with time was performed and is shown in Fig. 4. TOC analyses of the digester fluid indicated that a loss of 53.1 mmol l^{-1} of carbon

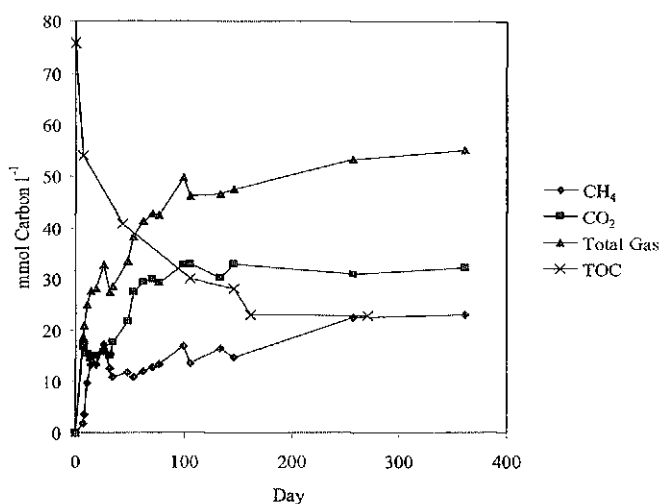


Fig. 4 Mass balance of mmol l^{-1} TOC degradation compared with the mmol l^{-1} Total Gas production, mmol l^{-1} CH_4 production, and mmol l^{-1} CO_2 production. Not shown is the 0.28 mmol l^{-1} carbon as biomass.

had occurred up to day 271. The TOC loss was accompanied by the production of 23.0 mmol l^{-1} of carbon as CH_4 , 32.3 mmol l^{-1} of carbon as CO_2 , and (not shown in Fig. 4) 0.28 mmol l^{-1} of carbon as biomass. The biodegradation resulted in 105% of the carbon being accounted for in the products, a value well within the experimental error in sampling and analysis.

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