

## Compound-specific carbon isotope analysis of a contaminant plume in Kingsford, Michigan, USA

**ROBERT L. MICHEL, STEVE R. SILVA, BRYAN BEMIS,  
E. MICHAEL GODSY, EAN WARREN**

*US Geological Survey, 345 Middlefield Road, Menlo Park, California 94025, USA*  
e-mail: [rlmichel@usgs.gov](mailto:rlmichel@usgs.gov)

**DAVID B. WESTJOHN**

*US Geological Survey, 6250 Mercantile Way, Suite 5, Lansing, Michigan 48911, USA*

**Abstract** Compound-specific isotope analysis was used to study a contaminated site near Kingsford, Michigan, USA. Organic compounds at three of the sites studied had similar  $\delta^{13}\text{C}$  values indicating that the contaminant source is the same for all sites. At a fourth site, chemical and  $\delta^{13}\text{C}$  values had evolved due to microbial degradation of organics, with the  $\delta^{13}\text{C}$  being much heavier than the starting materials. A microcosm experiment was run to observe isotopic changes with time in the methane evolved and in compounds remaining in the water during degradation. The  $\delta^{13}\text{C}$  values of the methane became heavier during the initial period of the run when volatile fatty acids were being consumed. There was an abrupt decrease in the  $\delta^{13}\text{C}$  values when fatty acids had been consumed and phenols began to be utilized. The  $\delta^{13}\text{C}$  value of the propionate remaining in solution also increased, similar to the results found in the field.

**Key words** contamination; groundwater; isotopes; methane

### INTRODUCTION

Anthropogenic contamination of groundwater by sewage and industrial chemicals has become a major source of concern in many areas of the world. Local officials and managers are frequently faced with trying to determine the source of contamination, and what the best management strategies are to limit or remedy the problems caused by them. Often a remediation programme is needed to rectify a contaminant problem before it affects important potable water supplies. In other cases, the contamination can be attenuated by natural processes, such as microbial degradation or dilution of the contaminant along the groundwater flow system. Even when natural processes reduce contamination, unexpected consequences and/or by-products may result in new problems that require treatment. One technique used to study organic compounds in groundwater is Compound-Specific Isotope Analyses (CSIA). Applying this technique, changes in the isotopic ratios of individual compounds can be measured along a flow path. With this information, it may be possible to determine the processes that are affecting the chemical concentrations in water and differentiate between microbial degradation and simple dilution (Hunkeler *et al.*, 1999). Here we discuss the application of this technique to a contaminated industrial site near Kingsford, Michigan, USA.

## SITE DESCRIPTION AND CHEMISTRY

In July 1995, a residence in Kingsford, Michigan exploded. Investigations by the US Environmental Protection Agency and other authorities led to the conclusion that the explosion was caused by an accumulation of methane gas in the residence from the underlying soil gas. Subsequently, other residences were evacuated due to high levels of methane found to be accumulating in them. Methane was found to be present in high quantities over an approximately 260 ha area, and outgassing of methane was found to be occurring in the Menominee River. Several potential carbon sources for production of methane were identified, including naturally occurring plant debris in Pleistocene sediments (~9000 BP), Precambrian graphitic Michigamme Slate, petroleum-based carbon compounds from waste pits, and wood-based waste products disposed of in waste pits. Data from  $^{14}\text{C}$  measurements of methane yielded ages of the order of a few hundred years old, which suggests that chemicals from wood disposal were the most likely source. Methane produced from petroleum products would be  $^{14}\text{C}$  free, while methane from debris in the sediments would have ages of several thousand years.

The area consists of layers of glaciofluvial sands over bedrock, that are separated by discontinuous layers of silt and clay. Groundwater generally flows in a westerly to southwesterly direction, flowing to the Menominee River (Fig. 1). Glacial kettles are present in the area and these features can furnish flow paths from the surface into the deeper glacial strata. Located approximately 1.6 km from the Menominee River is a manufacturing area that was used for the production of charcoal and organic compounds during the mid-1900s. Within the industrial site are glacial kettles, which were used as disposal sites for industrial chemicals, such as tars and creosotes.

The chemistry of groundwater in the area has been investigated as part of a series of studies since the mid-1980s. A wide array of organic compounds are found close to

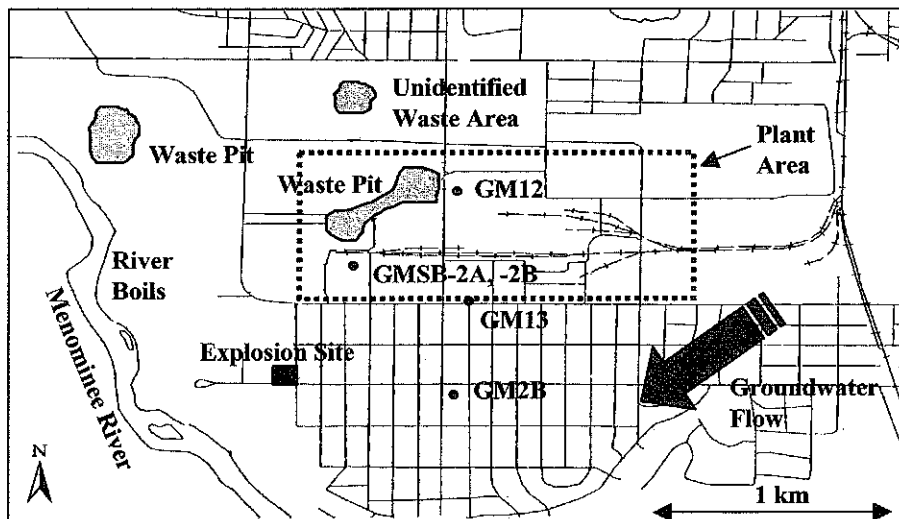


Fig. 1 Map of the site and well sites sampled.

the disposal site, with concentrations of three volatile fatty acids (VFAs), acetate, propionate, and butyrate, at greater than  $1 \text{ g l}^{-1}$  at some sites (Godsy *et al.*, 2001). These compounds along with other organic compounds are inhibitory to microorganisms at these concentrations so microbial activity is unlikely. However, as dilution occurs down the groundwater flow path, microbial degradation can occur. VFA concentrations decrease very sharply along the groundwater flow path, suggesting that microbial degradation progresses very rapidly once it begins. High dissolved methane concentrations ( $>60 \text{ mg l}^{-1}$  in some cases) are found southeast of the wood-waste disposal sites along the direction of groundwater flow (Westjohn *et al.*, 1997). Deuterium isotopic ratios for the methane were on the order of  $-300\text{‰}$  (per mil.). These are similar to isotopic ratios expected if the source of the methane is the fermentation of acetate (Revesz *et al.*, 1995). Dissolved oxygen and ferrous iron also support methane production by microbial degradation of organic compounds. However, other possible sources of organic compounds are also available in the vicinity, including a creek once used for the disposal of raw sewage, and other disposal sites that are not part of the industrial site. The US Geological Survey has studied the groundwater chemistry of the area to determine the likely source of the organic compounds. Microcosm experiments have also been carried out to determine if the chemical composition down gradient could be derived from the contaminant sites near the industrial disposal pits (Godsy *et al.*, 2001). This paper reports on CSIA of the organic compounds at selected sampling sites and in a microcosm using contaminated water from one of the sites.

## SAMPLING AND ANALYSIS PROGRAMME

Groundwater samples were collected from two sites representative of the chemicals in the contamination plume, and from one site where major changes in the chemical nature of the contamination had occurred, presumably due to microbial degradation (Fig. 1). GMSB2 is located approximately 300 m to the southwest of the presumed source, and consists of samples from two depths, 75 m (GMSB-2A) and 80 m (GMSB-2B). The two depths at this site are separated by a layer of fine sand, silt and clay. The chemical nature of the organic compounds is similar at both depths, containing about  $6 \text{ g l}^{-1}$  of VFAs and  $50 \text{ mg l}^{-1}$  of phenol compounds. GM13 (sample depth of 44 m) is located about 300 m south of the presumed source and is on a different flow path. Concentrations and the chemical makeup of the organics are similar to that at GMSB2. GM2B (depth of 83 m) is located about 800 m south of the presumed source. Concentrations and the overall chemical composition have changed significantly from the composition of the presumed source water. Propionate is the only VFA present in any significant quantity ( $1 \text{ g l}^{-1}$ ) and 3-ethylphenol is the only phenol compound present above  $1 \text{ mg l}^{-1}$ . More detailed discussions on the chemical changes at this site are found in Godsy *et al.* (2001).

Microcosm experiments were carried out using a mixture of 3.1 l of water from GMSB-2B and 0.75 l of anaerobic domestic sewage sludge. Details of the experiment are available in Godsy *et al.* (2001). CSIA was carried out on the residual organic compounds and the methane and carbon dioxide gas produced by the microbial reactions. Due to a leak in the microcosm bottle, no samples were collected during the

first 60 days. All dates given in this report use 28 November 1998 as day 1. Analyses were run by injecting samples into an HP 5890 gas chromatograph in series with a Micromass Optima mass spectrometer. Compounds in the water samples were extracted by first acidifying the water to a pH < 2, and then adding diethylether. A 10  $\mu$ l aliquot of the ether extraction was then injected into the gas chromatograph (0.25 mm ID, 30 m DB-WAXETR column with a 0.25  $\mu$ m thick coating). Samples were separated into individual compounds on the gas chromatograph and passed through a CuO furnace in the presence of excess oxygen where they were converted to CO<sub>2</sub>.

## RESULTS

### Water sample results

Results of CSIA measurements of the initial  $\delta^{13}\text{C}$  as ‰ of the major organic compounds at the three sampling sites are given in Table 1. As noted, the chemicals present in the groundwater are very similar for GMSB2A, GMSB2B and GM13. The isotopic data are also similar for most of the organic compounds present in the water samples. Carbon-13 data are essentially the same in all three samples for acetate, propionate and butyrate, averaging  $-29.6\text{‰}$ ,  $-19.6\text{‰}$  and  $-26.8\text{‰}$  respectively. All the  $\delta^{13}\text{C}$  data indicate a biological source for the organic carbon, which would be compatible with a source from the waste pits. The fact that the  $\delta^{13}\text{C}$  values are similar at all three sites is also compatible with one source for the organic compounds found in all three samples. Thus, the isotopic data support the chemical data in suggesting that there is a similar source for the contaminant, which is most likely the waste disposal pits and distillation area in the abandoned industrial complex. At GM2B, the  $\delta^{13}\text{C}$  of the propionate was significantly higher, being  $-14.2\text{‰}$ . There are small amounts of some phenols left, with the highest concentration being that of 3-ethylphenol which has an isotopic ratio of  $-14.8\text{‰}$ , which is also much heavier than the most phenols in the starting material.

**Table 1** Results of Compound-Specific Isotope Analyses of organic compounds from GMSB2A, GMSB2B, GM2B and GM13. There was insufficient acetate and butyrate at GM2B for analysis. The main phenol compound in each sample was measured as described below.

Well	$\delta^{13}\text{C}$ in ‰:			
	Acetate	Propionate	Butyrate	Phenol*
GMSB2A	-30.0	-18.9	-26.9	-27.0*
GMSB2B	-28.6	-18.9	-23.9	-27.1*
GM13	-30.1	-21.1	-29.4	-26.4*
GM2B		-14.2		-14.8†

\* 2-methylphenol.

† 3-ethylphenol.

### Microcosm results

Gas and water samples were analysed from the microcosm, although both types of samples were not collected on the same day. During the experiment, the VFAs were

degraded first, producing methane, which went into the gas phase, and carbon dioxide, which partitioned between the gas and liquid phase. The acetate and butyrate were completely utilized by the microbes during the first 61 days, before sample collection began. Insufficient amounts of these compounds were available for analysis after sampling began so no results are available for these compounds. Propionate and several phenols were left in the residual solution after 61 days and these were analysed for  $\delta^{13}\text{C}$ . Results of the  $\delta^{13}\text{C}$  analyses for samples collected during the microcosm experiment are shown in Fig. 2. Propionate was utilized preferentially by the microbes, and its concentration fell below the detection limit for samples collected after day 94. The methane and carbon dioxide were collected from the gas phase and the propionate was measured in extracts of the liquid phase.

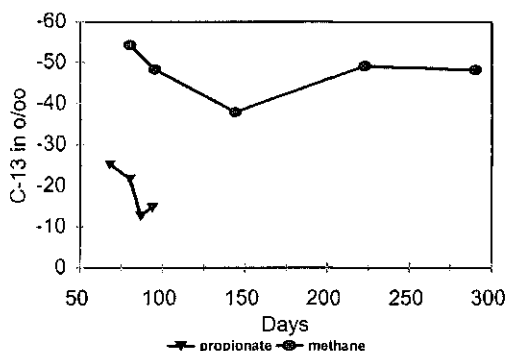


Fig. 2 Isotopic evolution of methane, carbon dioxide and propionate during the microcosm experiment.

## Discussion

Methane production, particularly by microbial processes, often results in  $\delta^{13}\text{C}$  values much lighter than the starting material (Bottinga, 1969; Shoell, 1980). Thus, the  $\delta^{13}\text{C}$  values of the residual carbon in solution, either as carbon dioxide, residual organic compounds, or both, will increase as the reactions progress. As microbial utilization of the residual carbon compounds continues, the isotopic composition of the methane produced should become heavier due to the process of Rayleigh distillation (Clark & Fritz, 1997). Thus, the  $\delta^{13}\text{C}$  of the methane in Fig. 2 should become less negative with time. Through the first 144 days of the experiment,  $\delta^{13}\text{C}$  in the methane produced by methanogenesis became heavier, increasing from  $-54.3\text{‰}$  on day 80 to  $-36.9\text{‰}$  on day 144. This is in keeping with Rayleigh distillation effects produced by the utilization of propionate by methanogenic microbes. The next gas sample collected at day 162 has a lighter  $\delta^{13}\text{C}$  value of  $-49.1\text{‰}$  and a sample collected at day 229 had a  $\delta^{13}\text{C}$  of about  $-48.3\text{‰}$ . The shift in the trend of the  $\delta^{13}\text{C}$  of the methane is undoubtedly the result of a switch in the organic compounds being utilized by the microbes (Godsy *et al.*, 2001). As has been noted, the first compounds used by the methanogenic consortium are acetate and butyrate. By the time samples were collected, propionate seems to have been the compound being utilized, and as will be discussed below, its  $\delta^{13}\text{C}$  increases with time. However, by approximately day 100 into the experiment, propionate and all

of the lower molecular weight VFAs have disappeared, and only higher weight chemicals such as the phenols were available to be metabolized. This change in the source chemicals also means that the  $\delta^{13}\text{C}$  of the starting material has changed and so the methane isotopic ratio will reflect this change. At this time, methane production also slowed noticeably (Godsy et al., 2001).

The  $\delta^{13}\text{C}$  of the carbon dioxide also increased from approximately  $-34\text{‰}$  to  $-20\text{‰}$  during the same period when VFAs were the primary source for methanogenesis.

The  $\delta^{13}\text{C}$  of the propionate tends to become heavier during the period between day 68 and day 87, increasing from  $-25\text{‰}$  to  $-12.8\text{‰}$  (Fig. 2). (There is a slight decrease in  $\delta^{13}\text{C}$  by day 93 to  $-14.8\text{‰}$  but this can be considered to be within the uncertainty of the measurements). The increase in the  $\delta^{13}\text{C}$  value of the propionate is the result of the production of the isotopically light methane. As lighter carbon goes into the gas phase in the form of methane, the heavier carbon remains with the residual propionate in solution, resulting in the higher  $\delta^{13}\text{C}$  values with time. The  $\delta^{13}\text{C}$  result for propionate from the microcosm duplicates the  $\delta^{13}\text{C}$  value for propionate found at site GM2B (Table 1). At this site, where the groundwater appeared to be most impacted by biological activity, the propionate, the only fatty acid available in any measurable concentration, had a  $\delta^{13}\text{C}$  value of  $-14.2\text{‰}$ . Thus, the isotopic data indicates that methanogenesis could be a process that would duplicate the data for propionate found at GM2B.

Carbon isotopic data were also obtained for several phenols during the microcosm work and most had  $\delta^{13}\text{C}$  values in the  $-25\text{‰}$  to  $-30\text{‰}$  range. Some phenols were not separable with the GC column used in this work and no definitive trends are apparent for any particular peak. The main point of interest is that the microcosm did not duplicate the reduction of the phenols to one peak as found at GM2B, and none of the peaks in the phenols obtained the relatively heavy  $\delta^{13}\text{C}$  value of  $-14.8\text{‰}$  found for the 3-ethylphenol at that site.

## REFERENCES

- Bottinga, Y. (1969) Calculated fractionation factors for carbon and hydrogen isotope exchange in the system calcite- $\text{CO}_2$ -graphite-methane-hydrogen and water vapour. *Geochimica et Cosmochimica Acta* **33**, 49-64.
- Clark, I. & Fritz, P. (1997) *Environmental Isotopes in Hydrogeology*. Lewis Publishers, Boca Raton, USA.
- Godsy, E. M., Warren, E. & Westjohn, D. (2001) Methanogenic biodegradation of charcoal production wastes in groundwater at Kingsford, Michigan, USA. In: *Impact of Human Activity on Groundwater Dynamics* (Proc. Symp. during Sixth IAHS Scientific Assembly at Maastricht, The Netherlands, July 2001). IAHS Publ. no. 269 (this volume).
- Hunkeler, D., Aravena, R. & Butler, B. J. (1999) Monitoring microbial dechlorination of tetrachloroethene (PCE) in groundwater using compound-specific stable carbon isotope ratios: microcosm and field studies. *Environ. Sci. Technol.* **33**, 2733-2738.
- Revesz, K., Coplen, T. B., Baedecker, M. J., Glynn, P. D. & Huit, M. (1995) Methane production and consumption monitored by stable H and C isotope ratios at a crude oil spill, Bemidji, Minnesota. *Appl. Geochem.* **10**, 505-516.
- Shoell, M. (1980) The hydrogen and carbon isotopic composition of methane from natural gas of various origins. *Geochimica et Cosmochimica Acta* **44**, 649-662.
- Westjohn, D. B. & Godsy, E. M. (1997) Microbial origin of methane in ground water and glacial deposits at Kingsford, Michigan. *US Geological Survey Administrative Report prepared for the US Environmental Protection Agency*, Chicago, Illinois, USA.