Determining BTEX Biodegradation Rates Using In Situ Microcosms at the Bemidji site, Minnesota: Trials and Tribulations

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ABSTRACT

In situ microcosms (ISMs) were installed in an aquifer contaminated by crude oil to study the in situ biodegradation of monoaromatic hydrocarbons. One was placed in an area where iron reduction predominates (ISM-Fe) and the other in an area where methanogenesis predominates (ISM-CH_4). Numerous problems were encountered during installation and operation of the ISM-CH_4 microcosm and therefore monitoring of it has been temporarily discontinued. Biodegradation rates determined from field concentrations suggested that degradation for the ISM-Fe should proceed in the following order: (1) toluene and *o*-xylene – ~12 days; (2) *m*-, *p*-xylene – ~400 days; (3) benzene – 700 days; (4) ethylbenzene – ~1600 days. Samples taken from the ISM-Fe at days 36 and 68 indicated that toluene biodegradation was occurring. Iron, manganese, CO_2, alkalinity, and low molecular weight volatile fatty acids increased while toluene concentration decreased by approximately 20 percent. All other organic and inorganic compounds remained at initial levels including the tracer with the exception of sodium, chloride, and sulfate. These species increased sharply starting at approximately day 8 and have remained elevated since then for an unknown reason.

INTRODUCTION

On August 20, 1979, approximately 1.7 x 10^6 liters (L) of crude oil was released in northern Minnesota due to a high-pressure pipeline rupture. At the completion of cleanup, 4.0 x 10^5 L of the oil remained. The majority of the oil pooled near the rupture site in the north pool while a smaller amount flowed overland to the southeast to a local depression and pooled to the south (fig. 1). At both sites, the remaining oil percolated through the unsaturated zone and pooled on the water table (Hult, 1984).

The fate, transport, and multiphase flow of the hydrocarbons present in the oil depend not only on geochemical processes, but also on volatilization, dissolution, biodegradation, transport, and sorption. All of these processes have been studied in detail by an interdisciplinary team from the U.S. Geological Survey and a number of universities.

The natural attenuation of water-soluble crude-oil organic due to biodegradation in the subsurface plume at Bemidji, Minn. is now well documented (Baedecker and others, 1993; Eganhouse and others, 1993, Essaid and others, 1995). In this paper we focus on the fate of a subset of the monoaromatic hydrocarbons: benzene, toluene, ethylbenzene, and *ortho*-, *meta*-, and *para*-xylene (BTEX). The major factor in the natural attenuation of the BTEX compounds is the ubiquitous degradative activity of the resident microbial populations. In order to formulate numerical models that simulate the transport and biodegradation processes, the biodegradation potentials and rates must be determined under naturally-occurring redox conditions.

The availability of electron acceptors is believed to determine the biodegradation potentials and rates of BTEX compounds. Availability and thermodynamic principles predict the sequence of electron acceptors used for biodegradation (Stumm and Morgan, 1981). The theoretical sequence is aerobic biodegradation, followed by denitrification,

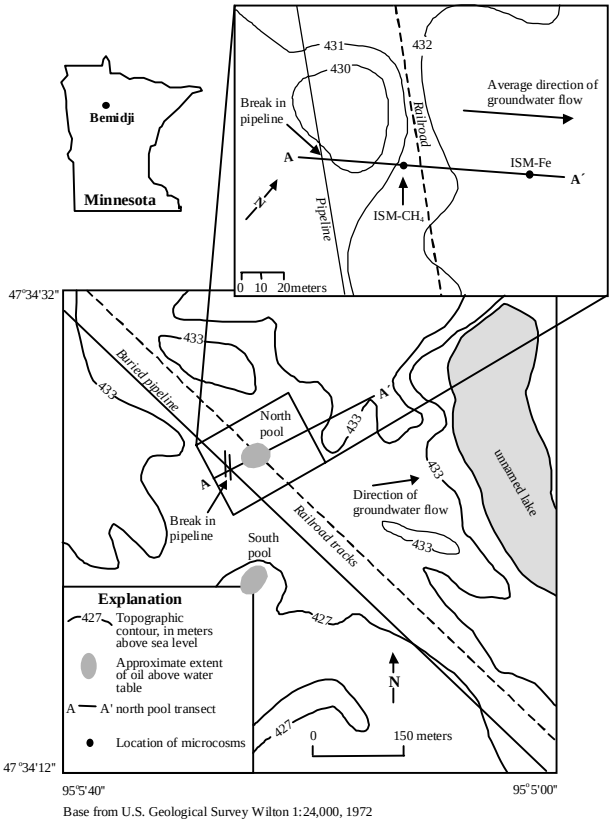

Figure 1. The study site at Bemidji, Minnesota, showing A-A´ transect, oil bodies, and oil pipeline.

manganese and iron reduction, sulfate reduction, and methanogenesis. This sequence has been shown to cause zonation in a contaminant plume with different electron accepting biodegradation processes dominating in different redox zones. At Bemidji, over fifteen years of observations have demonstrated that three redox zones predominate in the contaminant plume: (1) aerobic, (2) iron reducing, and (3) methanogenic (Baedecker and others, 1993; Bekins and others, 1999).

In situ biodegradation rates of the volatile organic carbon fraction at the site have been determined by fitting field concentrations using a two-dimensional reactive solute transport model with Monod biodegradation kinetics (Essaid and others, 1995). Monod kinetic constants for the individual BTEX compounds, determined by fitting field concentrations to a steady-state one-dimensional advective equation that incorporates Monod kinetics (Parlange and others, 1984), were used to predict time required for biodegradation of the individual BTEX compounds. We report here the results of an ongoing BTEX biodegradation experiment conducted with in situ microcosms (ISMs).

IN SITU MICROCOSM TECHNIQUE

The in situ microcosm (ISM) technique to determine biodegradation potentials and rates was developed at the University of Waterloo (Gillham and others, 1990a; Gillham and others, 1990b). The ISM consists of a stainless steel cylinder that encloses a volume of the aquifer that, once loaded with ground water spiked with specific hydrocarbon compounds, can be monitored over time for degradation. Unlike a field injection-tracer test where there is of the contaminant plume encountering areas of different redox potentials, differing microbial populations, and heterogeneity in the aquifer, this technique isolates a portion of the aquifer assuring the same conditions throughout the experiment.

Location of ISM

Both ISMs were placed along the A-A´ transect (figs. 1 and 2). The microcosm identified as ISM-CH_4 (borehole 9828) was placed in an area of the contaminant plume where biodegradation processes were predominately methanogenic. The top of the microcosm test chamber was set at an

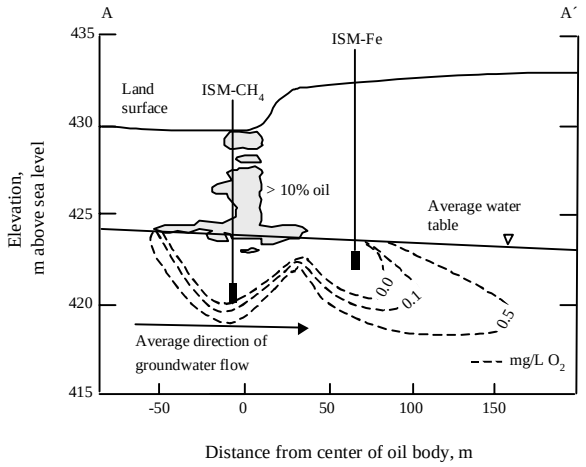

Figure 2. Cross section along transect A-A´ showing locations of the oil body, microcosms and concentrations of dissolved oxygen within the saturated zone, Bemidji, Minnesota.

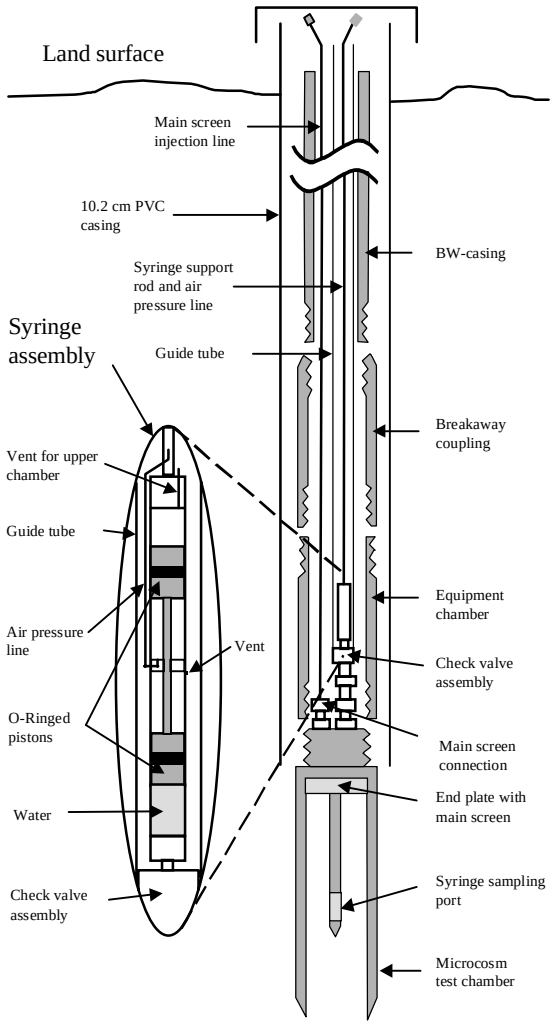

Figure 3. Cross section of the in-situ microcosm with an exploded view of the sampling syringe. Drawing not to scale.

elevation of 421.1 meters (m) above sea level. ISM-Fe (borehole 9825) was placed in an area where biodegradation was predominantly by iron-reduction and set at an elevation of 432.3 m above sea level (Bekins and others, 1999).

Description of ISM

The ISM consists of an 8.3 centimeter (cm) inside diameter (id) x 88 cm stainless steel cylindrical test chamber open at the bottom and bounded at the inside-top by a set of coarse and fine stainless steel mesh screens (fig. 3). The main screens are used to remove and reinject spiked ground water into the test chamber. The design allows even flow through the screens assuring plug flow into the test chamber during reinjection. The test chamber isolates a total aquifer volume of 4.76 L or 1.43 L of ground water (assuming a porosity of 0.3). A depth adjustable, stainless steel sampling port, with a fine mesh screen, extends 26 cm into the test chamber. Water samples are collected from the central port with a syringe assembly (see expanded section of figure 3).

The stainless steel syringe is 70 cm x 1.5 cm outside diameter (od) and was developed by Fred Murphy (U.S. Geological Survey, Menlo Park, Calif.). It is divided into two chambers – a lower 30 cm x 1.2 cm id water sampling camber and an upper compressed air chamber. The bottom of the syringe is fitted with a nipple (not shown in figure 3) that fits into and releases the spring-loaded ball in the check valve assembly for sample collection from the central spike port. Connected to the top of the syringe are 2 m lengths of 0.6 cm (od) stainless steel tubing that act as both the syringe support rod and the compressed air line.

An equipment chamber, threaded onto the top of the test chamber, protects the tubing connector and the syringe check valve assembly. A breakaway coupling with reverse threads adapts the equipment chamber to the lengths of BW-casing. A 6.4 millimeter (mm) Teflon tube for spiking and a polypropylene syringe guide tube (2.5 cm) connect to the ISM and pass through the large diameter metal (BW) casing to the surface.

Installation of ISM

The ISM and the attached BW casing were installed through the center of 15.2 cm hollow stem augers equipped with a wire-line, surface-connected knockout-plug in the cutting bit to prevent the cuttings from being carried up the interior of the augers. After drilling to the desired depth, the ISM was lowered through the augers until it rested on the knockout plug. The augers were pulled up slightly to allow the displacement of the knockout plug by the ISM. After the knockout plug was opened, the ISM was advanced into the undisturbed aquifer sediment using an electric vibrating hammer until the top of the test chamber was just below the bottom of the augers. A 10.2 cm PVC casing was then installed to the bottom of the augers and the augers removed leaving the ISM with sampling tubes and both the BW and PVC casings in place. The space between

the PVC casing and the aquifer sediment was filled with the drill cuttings.

Loading of ISM

Ground water was pumped from a nearby well that was screened at the target depth of the ISM (532 B for the ISM-CH_4 and 531 B for the ISM-Fe) until temperature and pH stabilized (approximately 5 casing volumes). At this time, 10 L of ground water was pumped into a 20 L Tedlar gas-sampling bag that was immersed in an ice filled picnic cooler. This was equivalent to approximately 7 ISM test chamber volumes. Prior to filling, the sampling bag was flushed five times with O_2-free Argon. The hydrocarbon and conservative tracer spike compounds were added carefully to the ground water in the sampling bag to exclude O_2. The hydrocarbon solution was thoroughly mixed and introduced by gravity into the ISM through the main screen injection line.

Sampling of ISM

Prior to sampling, the pistons were pushed to the bottom of each chamber by a set rod inserted in the upper chamber vent. The stainless steel syringe was then attached to the support tubing and adjusted to withdraw 10 milliliters (mL) of water. This was accomplished by placing a set rod in the upper chamber vent to stop the piston from travelling the complete 30 cm distance. Ten mL was determined to be the dead volume of the sampling port and check valve assembly. The syringe was lowered down the guide tube until reaching the check valve assembly. The syringe was then raised approximately 30 cm and jammed down into the check valve assembly. Approximately 400 kilopascals (kPa) of pressure was applied to the syringe from a portable air compressor. This compressed air displaced the pistons to the top of each chamber of the syringe. The lower chamber was simultaneously filled with a water sample from the microcosm. The dead volume was discarded. The set rod was removed and the syringe was again lowered to the ISM and a full 30 mL water sample was taken. The syringe was detached from the ISM by a gentle pull, elevated to land surface, and aliquots of the sample were transferred to the appropriate bottle by manually depressing the upper piston with a metal rod passed through the upper vent.

MATERIALS AND METHODS

BTEX Solution

The spiked ground-water solution could not be loaded into the ISM-CH_4 for unknown reasons;

Table 1. Concentations of compounds used in the BTEX solution for the ISM-Fe compared to the observed maximum field concentation in well 531 B at the Bemidji site, Minnesota.

	Concentration (µg/L)	
Compound	Maximum field	Spike solution
Benzene-D6	2100	2000
Toluene	10	1000
Ethylbenzene	323	650
m-xylene	78	250
p-xylene	78	250
o-xylene	20	150
isopropylbenzene	36	200
1-methyl-3-ethylbenzene	29	150
1-methyl-2-isopropylbenzene	6	100
1-methyl-4-isopropylbenzene	10	100
1,3-dimethyl-2-ethylbenzene	26	100
1,3-dimethyl-4-ethylbenzene	17	100
1,2,3,5-tetramethylbenzene	34	150
1,2,3,4-tetramethylbenzene	58	150

Table 2. Sampling scheme and methods for the ISM-Fe.

Parameter	Container	Bottle volume (mL)	Sample volume (mL)	Preservation (all chilled)	Analysis method
pH	Vial	5	2	None	Electrode
Alkalinity	Vial	5	2	0.2 μm nylon filter	Titration
Dissolved gases	Serum bottle, evacuated	10	2	$HgCl_2$	Headspace GC
Organic intermediates	Vial	5	10	Zero headspace	Acid ether extracct, GC/MS
BTEX compounds	Glass vial	5	5	$HgCl_2$, zero headspace	Purge & trap GC/MS
Fatty acids	Vial	5	2.5	$HgCl_2$	IC
Cations	Plastic bottle	10	4	0.2 μm nylon filter, 0.5% nitric acid	ICP/MS
Anions	Vial	5	2.5	0.2 μm nylon filter	IC

therefore, the composition of the solution is given only for the ISM-Fe (table 1). A hydrocarbon mixture was prepared in the laboratory by mixing the desired volumes of the neat compounds in an ampoule. A concentrated hydrocarbon solution was prepared in the field by injecting 59.5 microliters of this mixture into 200 mL of the ground water and mixing in a sonication bath for 60 min. Then, all of the concentrated solution was injected into approximately 10 L of ground water from well 531B. A conservative tracer, KBr was then added to a final concentration of 30 milligrams/liter (mg/L) as Br.

Sampling Protocol

Samples from ISM-Fe were analyzed for pH, alkalinity, intermediate organic acids, anions including low molecular weight volatile fatty acids (VFAs), cations, hydrocarbons, and dissolved CH_4 and CO_2 as outlined in table 2. Biodegradation rates determined from field concentrations suggested that the BTEX compounds for the iron reducing ISM should degrade in the following order: (1) toluene and *o*-xylene – ~12 days; (2) *m*-, *p*-xylene – ~400 days; (3) benzene – ~700 days; (4) ethylbenzene – ~1600 days. The sampling scheme was designed to obtain as many samples as possibly for each compound with in the limits of the total volume present in the ISM.

Analytical Techniques

Alkalinity was determined in the laboratory with an automatic titrator and pH was determined in the field with an electrode. The cations were determined using an ICPMS. Dissolved gasses were determined according to the method described Godsy and others (1992). The hydrocarbons were analyzed by purge and trap capillary gas chromatography with ion trap detection as described by Eganhouse and others (1999).

The anions and low-molecular weight fatty acids (formate, acetate, propionate, and butyrate; VFA) were determined using a Dionex Ion Chromatography System equipped with an advanced gradient pump with a conductivity detector, an anion self-regenerating suppressor with an autosuppression external water mode, and a 4 mm Dionex AS15 analytical column. The system was equipped with a guard column, a column heater set at 30°C, and an anion trap column.

Intermediate organic acids were determined by a single 2:1 acid extraction into diethylether. The extract was injected in a Finnigan GCQ GC/MS equipped with a 30 m x 0.25 mm (0.25 micrometer film) DB-WAXETR fused silica column (J&W Scientific, Folsom, Calif.). The oven temperature was programmed from 35 to 245°C at 8°C/min and held at the final temperature for 5 min. The injection port temperature was 265°C and helium carrier gas velocity was 40 cm/sec.

Table 3. Selected parameters and cations from the iron reducing ISM at the Bemidji site, Minnesota. All concentrations are in mg/L except for pH. Alk = laboratory alkalinity.

Time	pH	Alk	CO_2	CH_4	Fe	Mn	Na	K
Prespike	*6.95*	*503.7*	*233.7*	*4.90*	*1.30*	*3.07*	*4.91*	*2.56*
0	6.78	485.7	397.5	7.96	33.60	0.66	3.01	15.10
1	*6.90*	*497.0*	*357.1*	*5.58*	*15.90*	*0.70*	*3.83*	*16.13*
2	6.75	491.7	263.2	6.38	13.10	0.99	4.31	15.50
5	6.74	497.0	235.6	6.64	11.40	1.02	4.46	15.60
8	6.78	500.6	383.2	6.03	10.70	1.08	15.30	17.90
13	6.80	491.2	342.9	6.09	8.64	1.08	20.40	19.00
18	7.21	413.2	404.7	4.78	NS	NS	NS	NS
36	6.89	515.8	351.4	3.54	13.80	1.39	29.50	22.70
69	6.66	576.2	479.3	6.07	28.60	1.69	15.10	17.30

italics = average of 3 analyses
ND = not detected
NS = no sample

RESULTS

Anions and Cations

The pH, alkalinity, and concentrations of anions and cations for ISM-Fe are given in tables 3 and 4. Evidence that biodegradation was occurring by day 36 is given by the increase from day 13 in the terminal electron accepting cations Fe and Mn, and the increase from day 18 in alkalinity. The concentration of CH_4 remained constant over the experiment, but the VFAs, acetate, and formate, increased by day 36, and propionate increased at day 69.

The concentrations of the conservative tracers, K and Br, show some variability but did not decrease significantly over the experiment. It is of interest to point out that the concentrations of Na, Cl, and SO_4 increased dramatically after day 5. It is unknown why the concentration of these species would increase while the conservative tracers do not increase.

Table 4. Selected anions and low-molecular weight volatile fatty acids from the iron reducing ISM at the Bemidji site, Minnesota. All concentrations are in mg/L. Ace = acetate, For = formate, and Pro = propionate.

Time	SO_4	Cl	Br	Ace	For	Pro
Prespike	*4.58*	*3.13*	ND	*0.31*	*0.60*	ND
0	0.68	0.95	28.95	0.27	0.44	ND
1	*0.70*	*1.87*	*29.04*	*0.23*	*0.47*	ND
2	0.74	2.27	29.31	0.25	0.44	ND
5	0.71	2.31	28.82	0.26	0.44	ND
8	8.55	19.05	34.13	ND	ND	ND
13	11.97	30.65	37.56	ND	1.87	ND
18	17.52	NS	28.75	3.06	1.51	ND
36	19.51	43.47	32.20	ND	ND	ND
69	11.44	16.73	33.32	2.51	ND	0.74

italics = average of 3 analyses
ND = not detected
NS = no sample

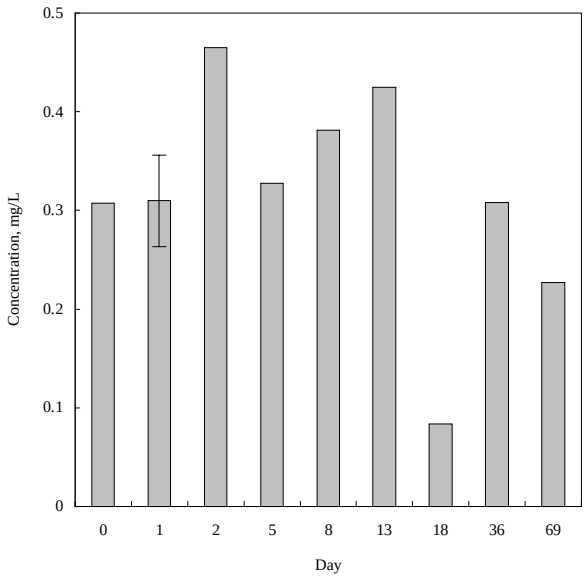

Figure 4. Concentrations of toluene in the ISM at the Bemidji site, Minnesota. Prespike concentrations were at method detection limit (MDL). Bar on day 1 represents the range of 3 replicates.

Organic Compounds

Over the course of the experiment only toluene showed any perceptible signs of biodegradation. Between days 13 and 69, there appeared to be a significant decrease in the amount of this compound (fig. 4) relative to the Br tracer. We have not established a sampling error at this time, and the next sampling is not scheduled until approximately day 170, at which time toluene degradation potential should be understood.

Benzoic acid, the major monoaromatic intermediate in the methanogenic biodegradation of monoaromatic compounds (Godsy and others, 1996) and presumably under iron reducing conditions, was detected on day 36, suggesting that biodegradation of monoaromatic hydrocarbons may be occurring in this time frame.

DISCUSSION AND CONCLUSIONS

The biodegradation of monoaromatic and polynuclear aromatic compounds under methanogenic conditions has been studied in detail in the last several years (Godsy and others, 1992; Godsy and others, 1996) and recently has been the subject of investigations under iron reducing conditions (Lovley and others, 1989). One of the questions surrounding the microbial ecology of the contaminant plume at the Bemidji site is the role of the individual members and the terminal member of the microbial consortia in different redox zones of the plume. Previous studies have shown that anaerobic iron reducing microorganisms can degrade some of the BTEX compounds in pure culture (Lovley and others, 1989; Lovley and Lonergan, 1990) while a consortia is required for these hydrocarbons under methanogenic conditions.

Investigations by Bekins and others (1999) into the nature of the microbial consortia at the Bemidji site have shown that iron-reducing microorganisms capable of utilizing acetate and H_2 as substrates are prevalent throughout the contaminant plume. They are present in both methanogenic and iron reducing redox zones, but are at lower numbers in the methanogenic zones. This finding, coupled with the appearance of VFAs and benzoate in the ISM-Fe suggests that the iron reducing microorganisms are acting as a terminal member of the consortium by utilizing the acetate and H_2 produced and not degrading the BTEX compounds directly. If the iron reducing microorganisms were degrading the BTEX directly, VFAs and benzoic acid would not appear as intermediates. Proof of this observation will require further study in the ISMs and in laboratory investigations.

Microorganisms in the zone of the plume where the iron-reducing ISM was placed have not previously encountered toluene or *o*-xylene in significant concentrations. In the past, these compounds have been degraded before reaching this distance down gradient in the aquifer (Eganhouse and others, 1993; Cozzarelli and others, 1994, Cozzarelli and others, 1999). The time elapsed for toluene biodegradation to begin, may be the time required for the microbial consortia to adapt to this compound. In addition, disturbance of aquifer material during installation may effect the degradation rate. It is not clear at this time whether a single microorganism is responsible for the ring cleavage of a single compound or its analogs or if a microorganism can open the ring structure of several classes of compounds. The preliminary results of the ISM suggest that the individual microorganism or consortia of microorganisms might be specific for a

limited number of compounds as was observed for creosote derived compounds (E.M. Godsy, unpub. data, 1993)

The reasons for the failure of the methanogenic ISM to accept the spike solution will remain a mystery until the ISM is recovered in the spring.

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