Paper 5A-01, in: A.R. Gavaskar and A.S.C. Chen (Eds.), *Remediation of Chlorinated and Recalcitrant Compounds—2004.*
Proceedings of the Fourth International Conference on Remediation of Chlorinated and Recalcitrant Compounds
(Monterey, CA; May 2004). ISBN 1-57477-145-0, published by Battelle Press, Columbus, OH, www.battelle.org/bookstore.

CHARACTERISATION AND REMEDIATION OF BROMINATED SOLVENTS AT A FORMER DIAMOND PROCESSING FACILITY

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ABSTRACT: Investigations at a former diamond processing facility established that tetrabromoethane, a dense liquid manufactured for use in heavy media separation, was the primary chemical used at the Site. However, the most prevalent chemicals detected in the subsurface were tribromoethene and dibromoethene. Subsequent investigations indicate that when the alkane tetrabromoethane is dissolved it degrades rapidly with a half life on the order of hours to days to form the alkenes tribromoethene and dibromoethene. At this stage, the degradation of tribromoethene and dibromoethene slows considerably and reductive debromination appears to be the dominant process for ongoing decay. Field investigations and preliminary laboratory testing suggest that several of the more common methods of remediation for chlorinated solvents may also be applicable to brominated solvents. The addition of molasses and ethanol to soil/groundwater microcosms appeared to have a limited success in decreasing the degradation half life of TriBE. The addition of zero valent iron, hydrogen peroxide and sodium hydroxide to soil/groundwater microcosms also significantly accelerated degradation of all the chemicals of interest. However, in the case of hydrogen peroxide and sodium hydroxide, secondary reaction products may limit the potential for in situ treatment of brominated solvents.

INTRODUCTION

Prior to its acquisition in 2000 by Argyle Diamonds, a mineral processing facility reportedly operated at the Site from about 1980 to 2000. It is understood that a range of chemicals were likely used during the operation of this facility, including tetrabromoethane (TBE). An inspection following the takeover of the Site in 2000 identified the possibility of laboratory-related chemicals reaching the subsurface through a failure of the building drainage system. The existence of specific brominated chemicals in soil and groundwater was identified through subsequent investigations.

BACKGROUND

The Site is located on the Swan Coastal Plain in Perth, Australia and is underlain by about 20 metres of superficial sediments. The superficial sediments are generally composed of stratified sands with subordinate silty sands. A relatively narrow zone (less than one metre thickness) of clayey sands, thin clay layers and shelly calcarenite is located near the base of the superficial sediments. This was underlain by relatively homogenous coarse sand that extended to a depth of more than 30 metres in the area of the Site.

The groundwater table at the Site is located at a depth of about 2 metres below ground surface. Groundwater flow is to the west northwest toward a surface water receptor (Belmont South Drain), which is located about 180 metres from the Site. The groundwater velocity is estimated to be between 20 and 40 metres per year. Geochemical conditions are mildly reducing and dissolved iron concentrations of about 2 mg/L have been observed.

INVESTIGATIONS CONDUCTED

Following the initial inspection by Argyle, a series of progressively more focused investigations were conducted. The investigations consisted of sampling and testing of soil, groundwater, surface water, soil vapour and ambient air in the area of the Site over four stages during a period of about two years. Investigations were first focused on identifying the extent of the source area and on refining the chemicals of interest at the Site. Later stages of work were focused on defining the extent of the chemicals of interest in groundwater hydraulically down gradient of the Site and on establishing risk-based investigation criteria for the protection of human health and the environment.

Specifically, the investigations conducted that are relevant to this paper included:

- Regular sampling of groundwater and surface water over a period of about 18 months (August 2002 to December 2003)
- Development of risk-based criteria for the chemicals of interest to protect potential ecological and human health receptors in the area of the Site
- Preliminary laboratory microcosm and column testing to evaluate the natural fate of chemicals at the Site as well as the effect of several possible remedial approaches including exposure to zero valent iron, hydrogen peroxide, sodium hydroxide, molasses and ethanol.

RESULTS

Chemicals of Interest. As the history of the Site was initially not well known, samples of soil, groundwater, surface water, soil vapour and ambient air were collected and analysed for a wide spectrum of chemicals. These analyses included typical volatile and semi-volatile organic compounds, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons, organochlorine pesticides, amines and ketones. In addition, wide spectrum analytical scans were also conducted with the intent of identifying atypical chemicals that were present in the samples. It was as a result of this wide spectrum analyses that the brominated chemicals TBE, tribromoethene (TriBE), dibromoethene (DBE) and vinyl bromide (VB) were identified as the primary chemicals of interest at the Site.

Chemical Distribution. The distribution of the chemicals of interest at the Site can be separated into two main zones. The first, termed the source zone, is located in the vicinity of a floor drain at the former facility and is characterised by the highest concentrations of all chemicals of interest. The source zone appears be limited to a localised area of about 10 m in diameter and is present between the water table (about 2 m below ground surface) and a depth of about 16 m. Groundwater sampling from the vicinity of the source zone indicates that TBE in the form of a dense, nonaqueous-phase liquid (DNAPL) is likely to be present.

The second zone of contaminated groundwater is located hydraulically down gradient of the source zone over relatively the same depth interval. This groundwater plume consists primarily of dissolved phase TriBE and DBE. VB was also detected in this zone but at much lower concentrations than those detected in the source zone.

CHEMICAL FATE

Tetrabromoethane. A summary of the measured concentrations in monitoring wells along the approximate centreline of the dissolved plume is presented in Table 1. These results indicate that TBE was only detected within the source zone, despite the location of several wells only a few metres hydraulically down gradient. The identification of TBE was not unexpected as significant quantities of this chemical had been reportedly used at the Site. TBE, an alkane, is an uncommon industrial chemical that is manufactured for use predominantly in heavy media separation (Montgomery, 2000).

The primary chemical of interest detected in the subsurface at the Site was TriBE. The identification of TriBE and DBE, both alkenes, was at first perplexing as both are rarely manufactured, have no known industrial use and have a dissimilar chemical structure to TBE. The results suggested that TBE, an alkane, was degrading rapidly (half life on the order of hours to days) to form the alkenes TriBE and DBE. This had been reported previously in groundwater elsewhere in the Perth area (Heitz et al, 1997). This same degradation pattern was subsequently observed in preliminary microcosm testing using soil and groundwater from the Site. In the microcosm tests, complete degradation of dissolved TBE was observed over a period of a few hours (CSIRO, 2003).

TABLE 1. Summary of brominated solvent concentrations at selected locations

Location	Flow Dist. (m)	No. of Events	TriBE (µg/L)			DBE (µg/L)			VB (µg/L)		
			Min	Max	Avg	Min	Max	Avg	Min	Max	Avg
MB01B	0	10	9800	>470000	198500	760	3800	2400	0.9	<100	26
MB09B	40	9	5200	>160000	57700	750	5800	3190	<0.1	<100	30
MB15B	70	8	850	24000	7970	50	2600	1280	<0.1	770	180
MB35B	180	5	1400	6600	3880	1300	3100	2440	19	85	51
MDS01	185	9	<0.1	0.50	0.1	0.28	1.90	0.7	<0.1	0.75	0.2

Notes.

1. All samples were collected from monitoring wells except MDS01, which was surface water
2. TBE - tetrabromoethane, TriBE - tribromoethene, DBE - dibromoethene, VB - vinyl bromide
3. TBE was not detected in groundwater at any other location other than MB01B
4. TBE concentrations at MB01B ranged from <50 to 69000 µg/L with an average of 20880 µg/L
5. SW - surface water
6. AVG - average of measured concentrations between August 2002 and December 2003
7. Where concentrations were reported greater than a value, the value was used in calculating the average
8. Where concentrations were reported less than a value, half of the value was used in calculating the average

Tribromoethene, Dibromoethene and Vinyl Bromide. The approximate extent of TriBE dissolved in groundwater at the Site is presented on Figure 1. A graphical representation of the molar percentage of the chemicals of interest in groundwater at different distances from the source zone is presented on Figure 2. These results indicate that the molar ratio of DBE to TriBE increased with increasing distance from the source. Similar results were also observed in the laboratory microcosm tests where the molar ratio of DBE to TriBE increased over time (Cohen et al., 2003). These results suggest that reductive debromination of TriBE to DBE is occurring in the groundwater.

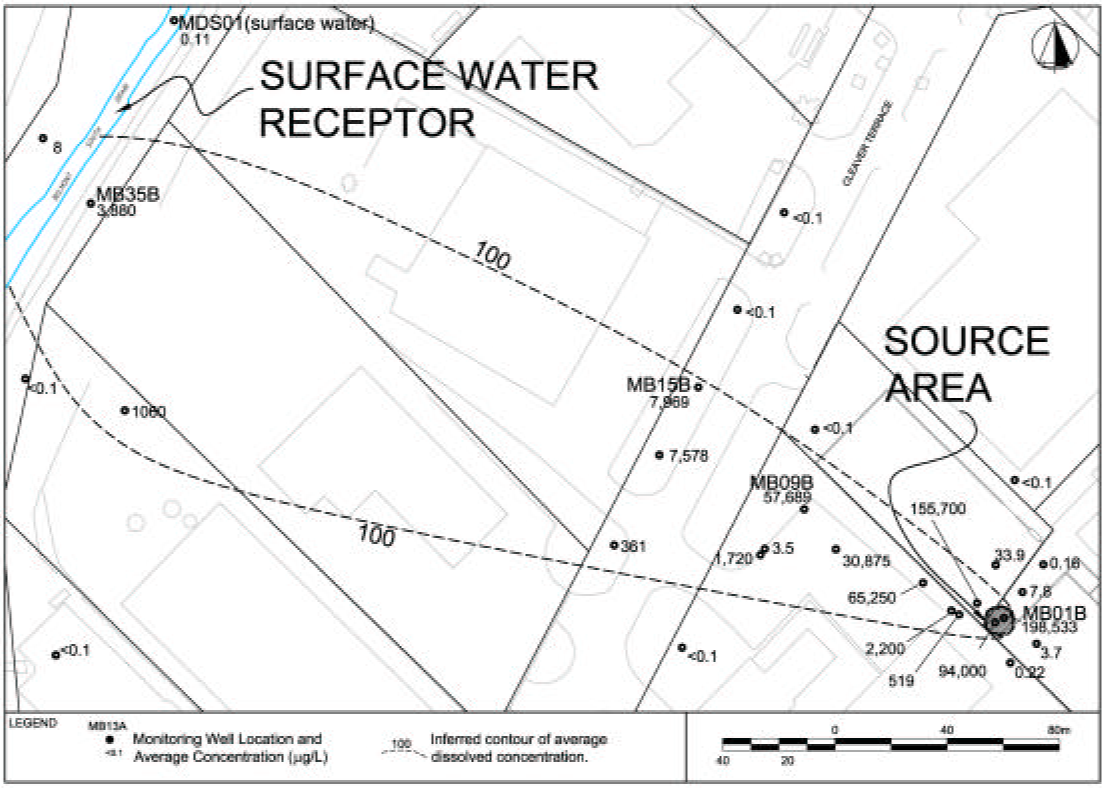

FIGURE 1. Average concentrations of tribromoethene in groundwater and surface water.

The data presented on Figure 2 also indicate that the ratio of VB to TriBE and DBE does not significantly change in groundwater. These results taken in conjunction with the constant occurrence of DBE in surface water located hydraulically down gradient of the Site suggest that degradation of DBE may be quite slow in comparison to TBE and TriBE.

In contrast to groundwater, the molar ratios of VB to TriBE and DBE in samples collected from the surface water receptor located hydraulically down gradient of the Site show a significant increase. However, the concentrations of the chemicals of interest observed at this location were generally near laboratory detection limits and the observed increase in the VB molar ratios may not be statistically significant.

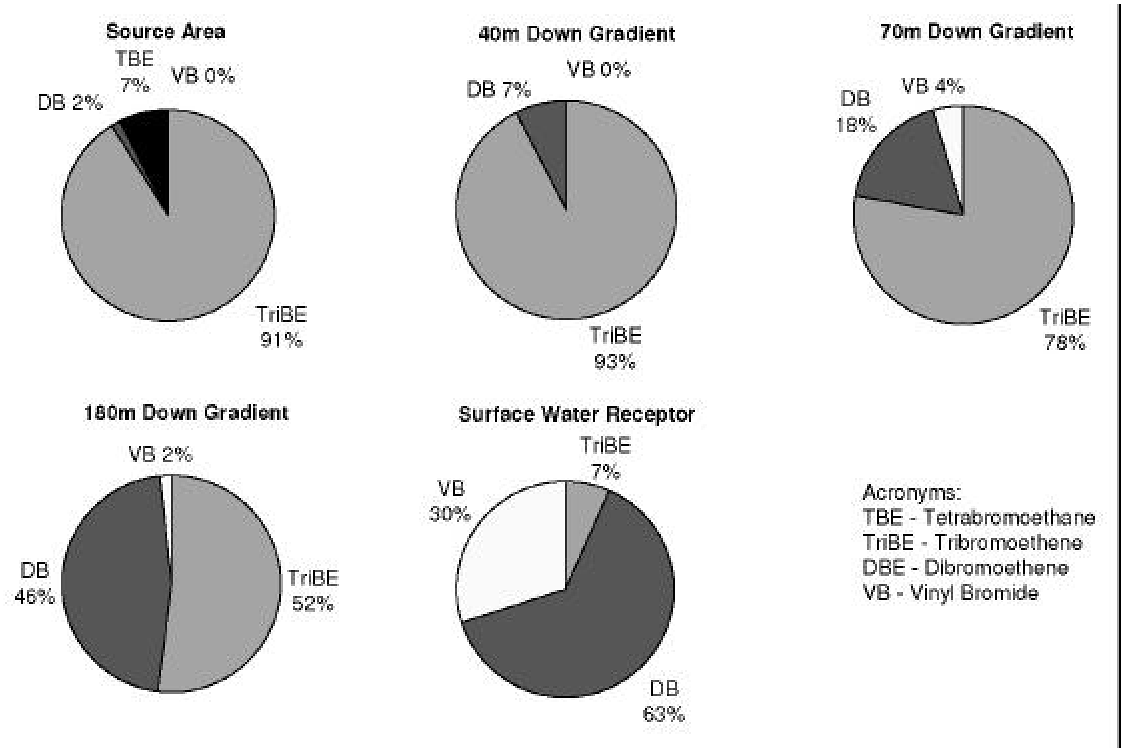

FIGURE 2. Molar sercentage distribution of brominated compounds in groundwater.

PRELIMINARY EVALUATION OF REMEDIAL TECHNOLOGIES

Argyle Diamonds is presently implementing a remediation strategy to address risks to current and future beneficial uses of the groundwater consistent with current and future land-use zoning, and to allow reuse of the site for continuing commercial/industrial purposes.

In order to aid in the selection of potential remediation and treatment methods for groundwater at the Site, a series of microcosm and column experiments were conducted. These experiments considered the degradation rates and products of TBE using soil and groundwater collected from the Site. A variety of treatments were considered including exposure to zero valent iron, molasses, ethanol, sodium hydroxide and hydrogen peroxide. The degradation half lives for TriBE and DBE that were observed for each of the treatments are presented in Table 2. A brief discussion of the results of this preliminary work and the potential implications to remediation of the Site is presented below.

Natural Attenuation. The results of the microcosm work indicated that TBE degradation was rapid in the presence of soil or groundwater from the Site with measured half lives of 0.2 days or less. The only microcosm that did not show rapid TBE degradation was a mixture of TBE with distilled water (no soil or groundwater). This suggests that groundwater and soil from the Site enhance the degradation of TBE to TriBE and DBE. However, both the microcosm experiments and field observations indicate that once TriBE and DBE are formed, natural degradation rates are quite slow, with half lives on

TABLE 2. Observed degradation half lives for tribromoethene and dibromoethene

Treatment	Observed Half Life (Days)	
	TriBE	DBE
Natural Attenuation	>100	-
Ethanol Amended	>100	-
Molasses Amended	48	-
Zero Valent Iron	0.8	4
Hydrogen Peroxide	0.5	1
Sodium Hydroxide	0.2	1

the order of a hundred days or more. The results of the microcosm experiments were also similar to field observations in that a significant increase of VB was not observed as a result of degradation of TriBE or DBE, which further supports the hypothesis that DBE degradation may be a rate limiting step under natural conditions.

Zero Valent Iron. Preliminary results of the microcosm experiments suggest that the brominated chemicals of interest are rapidly degraded in the presence of zero valent iron. Observed half lives were less than one day for TriBE and four days for DBE. The experiments also showed that the accumulation of DBE and VB was much less than would be predicted from the degradation of TriBE. In the case of VB, no substantial accumulation was observed. This observation is consistent with the results from similar chlorinated systems (Gillham and O'Hannesin, 1994).

Molasses and Ethanol Amended Degradation. Preliminary results of the microcosm experiments indicate that amended degradation through the addition of molasses or ethanol was only marginally successful. In the case of ethanol, no increase in degradation rate was observed between the amended microcosm and the control. In the case of molasses, a gradual decline of concentrations of TriBE was observed along with the formation of DBE and VB. However, the observed half life for TriBE in the molasses amended microcosm of 48 days was, while faster than the control, still relatively slow compared to some of the other remediation methods. Reductive debromination of vinyl bromide by *Dehalococcoides* sp. BAV-1 has been recently reported (He et al, 2003) but biological transformations of TriBE and DBE are unknown.

Chemical Treatment. The chemical treatment microcosms showed the most significant reduction of all brominated chemicals of interest. For both hydrogen peroxide and sodium hydroxide, the observed degradation half life for TriBE was less than one day. In addition, significant quantities of DBE or VB were not observed, which suggested that degradation was both rapid and complete. However, oxidation with hydrogen peroxide resulted in the production of bromate, which is classified by the United States Environmental Protection Agency as a probable carcinogen and has a maximum contaminant level (MCL) of 10 µg/L. Both of these treatments may result in potentially harmful by-products or undesirable changes in water quality which would limit their usefulness as in situ treatments.

Hydraulic Manipulation. Sorption experiments were conducted in small-scale columns with aquifer sand from the site to determine retardation coefficients of TriBE and DBE. Preliminary results from the column tests indicate that these chemicals are only slightly sorbed (an initial estimate of a retardation coefficient for both TriBE and DBE was about 1.1). This result, in combination with the relatively high solubility of TriBE (observed to be in excess of 200 mg/L in both the field and the laboratory) suggests that hydraulic manipulation could be an effective means of control and/or removal of the chemicals of interest in groundwater.

IMPLICATIONS

TBE, an alkane, was historically used at the Site. However, the most prevalent chemicals detected in the subsurface where the alkenes TriBE and DBE, which are considered to be degradation products of TBE. Subsequent investigations indicate that when TBE is dissolved it degrades rapidly with a half life on the order of hours to days to form TriBE, DBE and VB. As all of these compounds are uncommon and are not generally considered for site characterisation, a modified analytical program including both brominated alkanes and alkenes should be considered if TBE use is suspected. In addition, if TriBE is present in groundwater, the absence of dissolved TBE does not exclude the presence of a TBE DNAPL source.

The results of field investigations and preliminary laboratory testing suggest that several of the more common methods of remediation for chlorinated solvents may also be applicable to brominated solvents. However, several potential issues that are unique to the treatment of the brominated chemicals of interest were identified which will require additional consideration. The addition of molasses and ethanol to soil/groundwater microcosms appeared to have a limited success in decreasing the degradation half life of TriBE. The addition of zero valent iron, hydrogen peroxide and sodium hydroxide to soil/groundwater microcosms did result in significantly accelerated degradation of all the chemicals of interest. However, in the case of hydrogen peroxide and sodium hydroxide, secondary reaction products may limit the potential for in situ treatment of brominated solvents.

REFERENCES

Budavari, S. (Editor). 1996. *The Merck Index. An Encyclopedia of Chemicals, Drugs and Biologicals. 12th Edition*. Merck and Company, Whitehouse Station, NJ, USA.

Cohen, E. L., Patterson, B.M., and Robertson, B.S. 2003. *Laboratory Testing Program for Tetrabromoethane Remediation: Stage 1, Microcosm Experiments.* A Confidential Report to Argyle Diamonds. CSIRO Land and Water, Perth, WA, Australia.

Cohen, R.M. and J.W. Mercer (Editors). 1993. *DNAPL Site Evaluation*. CRC Press, Inc. FL, USA.

Gillham, R.W. and O’Hannesin, F.O. 1994. “Enhanced Degradation of Halogenated Aliphatics by Zero Valent Iron”, *Ground Water*, 32 (6): 958-967.

He, J., K.M. Ritalahti, K. Yang, S.S. Koenigsberg and F.E. Löffler, 2003. "Detoxification of vinyl chloride to ethene coupled to growth of an anaerobic bacterium". *Nature*, 424: 62-65.

Heitz, A., R. Alexander and R.I. Kagi, 1997. "Formation of Brominated Ethylenes from 1:1:2:2-Tetrabromoethane in Groundwater." In Horsfield B. (ed.), *Proceedings of the 18th International Meeting on Organic Geochemistry*. *pp. 65-66*. Forschungszentrum, Julich, Germany.

Howard, P.H. 1993. *Handbook of Environmental Fate and Exposure Data for Organic Chemicals*. *Volume IV, Solvents 2*. Lewis Publishers, MI, USA.

Montgomery, J.H. 2000. *Groundwater Chemicals Desk Reference*, *Third Edition*. CRC Press, Inc. FL, USA.

SRC (Syracuse Research Corporation) 2002. The *Physical Properties Database (PHYSPROP)*. http://esc.syrres.com/interkow/PhysProp.htm.

United States National Library of Medicine. 2002. *The TOXNET Network of Databases on toxicology, hazardous chemicals, and related areas*. http://toxnet.nlm.nih.gov/.

United States Environmental Protection Agency (USEPA). 2002. *ECOTOX User Guide: ECOTOXicology Database System, Version 2.0.* http://www.epa.gov/ecotox/.

United States Environmental Protection Agency (USEPA). 2003. *National Primary Drinking Water Standards*. http://www.epa.gov/safewater/mcl.html.

Verschueren, K. 1983. *Handbook of Environmental Fate Data on Organic Chemicals. 2nd Edition.* Van Nostrand Reinhold Company, Inc. NY, USA.