Bull. Environ. Contam. Toxicol. (1990) 45:507–515

Bulletin of Environmental Contamination and Toxicology

Determination of Trace Concentrations of Volatile Organic Compounds in Ground Water Using Closed-Loop Stripping, Edwards Aquifer, Texas

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The Edwards aquifer in the Cretaceous Edwards Limestone in south-central Texas (U.S.A.) is the sole source of drinking water for San Antonio (the tenth largest city in the U.S.A) and is the major source of water for much of the region (Figure 1). The aquifer is a highly permeable, dissolution-modified, faulted limestone. The areas that are considered most susceptible to contamination from surface sources are the aquifer outcrop and the part of the aquifer downdip from the outcrop that is unconfined (collectively known as the recharge area) (Figure 1). Septic-tank seepage from individual residences and underground gasoline-storage tanks in the recharge area pose a substantial potential for ground-water contamination. Several volatile organic compounds have been found intermittently in concentrations at or greater than analytical detection limits of 3 µg/L (Reeves and Ozuna 1986; Ozuna et al. 1987) and 1 µg/L (Buszka 1987) in water from the San Antonio segment of the Edwards aquifer. These detections mainly have been in samples from wells in the recharge area of the aquifer.

This report presents the results of a study to verify whether volatile and semivolatile organic compounds occur at less than microgram-per-liter concentrations in the Edwards aquifer, and to assess the potential use of such compounds for regional tracers of ground-water quality. The scope of this study is limited to the part of the aquifer between and including San Antonio and Austin.

MATERIALS AND METHODS

Water samples were collected from four wells in the recharge area of the Edwards aquifer and at Comal Springs, a major discharge from the confined zone (Figure 1). Wells AY-68-28-202 and YD-58-42-813 are in residential areas serviced by septic systems. Wells AY-68-27-303 and YD-58-50-215 are in areas with a lower density of residential development and lie along different flowpaths than the other sites. Samples collected from Comal Springs (DX-68-23-301) represent the water chemistry of a highly transmissive part of the confined zone. Duplicate samples were collected from wells AY-68-

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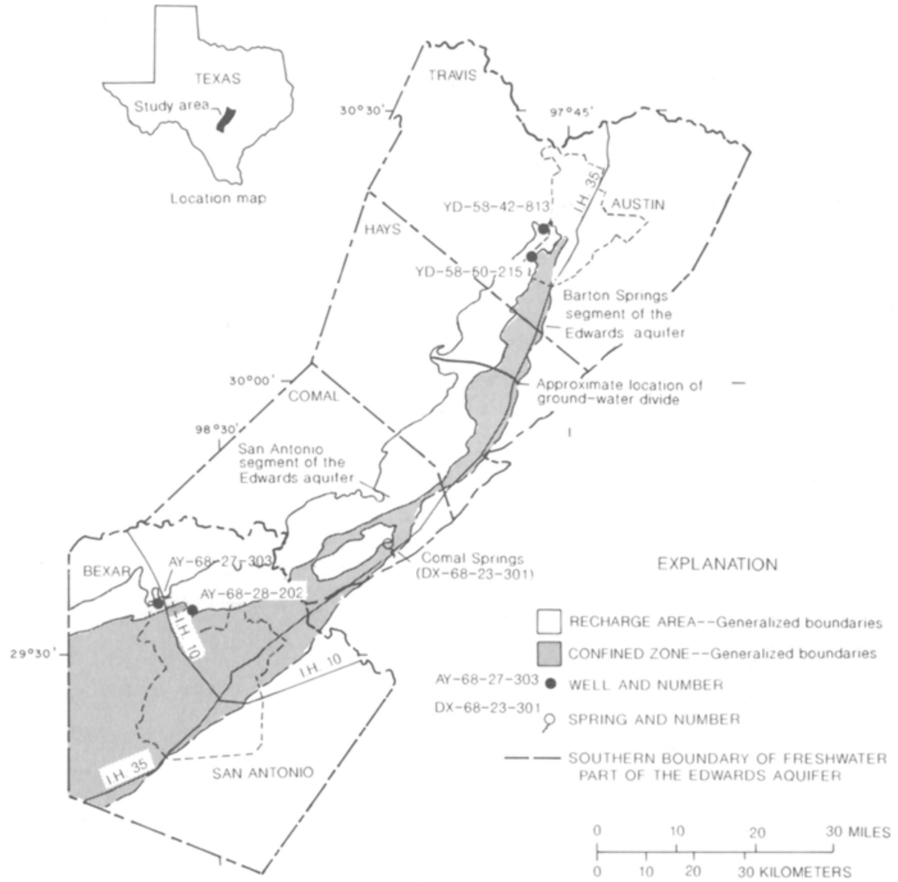

Modified from Maclay and Land 1988
and Slade et al. 1986

Figure 1.--Location of the Edwards aquifer in the San Antonio and Austin regions and of wells and spring sampled during this study.

28-202 and YD-58-50-215, and triplicate samples were collected from well YD-58-42-813.

The samples for organic analysis were collected in clean, 4-L amber glass bottles with Teflon[1]-lined screw caps. Each well was pumped for a minimum of 30 min prior to sample collection. Samples were collected from a faucet at the well head after specific conductance, pH, and temperature stabilized. The bottles were flushed with three volumes of sample water prior to collection, filled without headspace, and refrigerated at 4 °C until analysis. At Comal Springs, samples were collected by submerging the bottles and allowing water to enter until no headspace remained. Two surrogate standards, 1-chlorohexane (C6Cl) and 1-chlorooctadecane (C18Cl), were injected into the samples before they were sealed to evaluate losses of organic compounds during shipment and storage. An internal standard, 1-chlorododecane, also was injected into the sample at the same time for calculation of concentrations of tentatively-identified compounds.

This study used closed-loop stripping (CLS) to extract (Grob and Zurcher 1976; Barber 1985), and gas chromatography/mass spectrometry (GC/MS) to separate, identify, and quantify organic compounds in water. Four-L samples were sparged for 2 hr. Compounds stripped from the water were trapped on a 1.5-mg activated-carbon filter and then eluted with 20 μL of methylene chloride. An internal standard, 1-chlorooctane (C8Cl), was added to the methylene chloride extracts before GC/MS analysis. Analysis of the extracts was performed on a Hewlett-Packard 5985 GC-MS system equipped with a capillary column (5% phenylmethyl silicone), using a helium carrier gas. One μL of extract was injected splitless at 275 °C. The column temperature (30 °C at injection) was held for 10 min, increased to 300 °C at 6 °C per min, and then held at 300 °C for 5 min. Mass spectra were acquired from 50 to 450 atomic mass units at 2 scans per second.

Tentative compound identifications from GC/MS analyses were based on computer matching of sample mass spectra with those of the National Institute for Standards and Technology library. Concentrations were calculated relative to 1-chlorododecane using total ion peak areas and assuming a relative response factor of 1. The 1-chlorododecane standard was not recovered from extracts from Comal Springs samples, and concentrations were calculated using the lab-fortified internal standard, 1-chlorooctane, again assuming a relative response factor of 1. A study of the recovery of 1-chlorododecane by CLS extraction of 4-L water samples determined a mean recovery of 81% and a relative standard deviation of 23% (Barber 1985).

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[1] Use of brand and firm tradenames in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

RESULTS AND DISCUSSION

Recovery data from the surrogate standards indicate that an unknown quantity of volatile compounds was lost during sample storage and transfer (Table 1). The small recovery for 1-chlorooctadecane probably is due to sorption to the glassware and its lesser volatility compared to the other standards. Recoveries of 1-chlorohexane also were small compared to 1-chlorododecane, possibly indicating volatilization-related losses from the samples.

Table 1.--Summary of surrogate standard recovery data from closed-loop stripping and gas chromatography/mass spectrometry analysis of water samples (Percent recovery with respect to 1-chlorododecane standard).

Local well or spring ID	1-chlorohexane	1-chlorooctadecane
AY-68-27-303	81	D.
AY-68-28-202	42	D.
	70	D.
DX-68-23-301	N.D.	N.D.
(Comal Springs)	N.D.	N.D.
YD-58-42-813	45	D.
	25	32
	21	N.D.
YD-58-50-215	N.D.	N.D.
	37	54

[D., surrogate standard detected in sample by extracted ion current profile (EICP) method; N.D., surrogate standard not detected in sample by EICP method]

Several compounds classified as priority pollutants by the U.S. Environmental Protection Agency (EPA) (1987) were detected in water from the Edwards aquifer using the CLS method (Table 2). Tetrachloroethene (PCE) was detected in all samples collected from Comal Springs and from the two recharge-area wells in areas with septic sewers (AY-68-28-202 and YD-58-42-813). Methyl benzene (toluene) was detected in one of two samples from wells AY-68-28-202 and YD-58-50-215 and in one of three samples from well YD-58-42-813. A dimethyl benzene (xylene) isomer was detected in one of two samples from well YD-58-50-215. Inconsistency of toluene and xylene detection among replicate samples in combination with losses of surrogate compounds indicate biodegradation as a probable cause for the losses. Consistent detection of PCE, a compound with a greater volatility and greater resistance to biological transformation, also supports this hypothesis. Trichloro-

Table 2.--Volatile and semivolatile organic compounds in water samples from selected locations in the Edwards aquifer and in an analysis of rainwater from Los Angeles, California

[ng/L, concentration in nanograms per liter; --, analysis not performed; <, less than reporting limit shown; (10), compound detected in sample in concentration less than reporting limit of 10 ng/L]

Local well identification	Date sampled (YYMMDD)	Compound name	Closed-loop stripping concentration (ng/L)	Purge-and-trap concentration (ng/L): year sampled
AY-68-27-303	870915	No target compounds detected		
		1,1'-thiobis-benzene	90	--
AY-68-28-202	870729	Methyl benzene (toluene)	30	<200 : 1987
		Tetrachloroethene	30	<200 : 1987
AY-68-28-202	870729	Tetrachloroethene	60	<200 : 1987
DX-68-23-301 (Comal Springs)	870707	Tetrachloroethene	60	<200 : 1988
DX-68-23-301 (Comal Springs)	870729	Trichloroethene	40	<200 : 1988
		Tetrachloroethene	90	<200 : 1988
YD-58-42-813	871001	Tetrachloroethene	40	<3,000 : 1988
YD-58-42-813	871001	Methyl benzene (toluene)	10	<3,000 : 1988
		Tetrachloroethene	30	<3,000 : 1988
YD-58-42-813	871001	Tetrachloroethene	20	<3,000 : 1988
		2,6-bis-di-tert-butyl-p-benzoquinone	20	--
YD-58-50-215	870708	Methyl benzene (toluene)	40	<3,000 : 1988
		Dimethyl benzene (xylene)	80	<3,000 : 1988
		2,6-bis-di-tert-butyl-p-benzoquinone	30	--
YD-58-50-215	870708	2,6-bis-di-tert-butyl-p-benzoquinone	(10)	--
Selected compounds from a rainwater analysis, Los Angeles, CA (Kawamura and Kaplan 1983)	820326	Tetrachloroethene	--	21
		Methyl benzene (toluene)	--	76
		Dimethyl benzene (xylene)	--	11

ethene was detected in one sample from Comal Springs. These compounds were not detected in the set of reagent blanks run during the study to identify sources of analytical interference.

The maximum concentration of PCE detected using CLS was 90 ng/L at Comal Springs. This concentration is about one-fiftieth of the maximum contaminant level (MCL) of 5 μg/L currently proposed by the EPA (1987). The maximum concentrations measured for toluene (40 ng/L) and xylene (80 ng/L) were detected in a sample from well YD-58-50-215. These concentrations were nearly five orders of magnitude less than the MCL of 2 mg/L currently proposed for both compounds by the EPA (1987). The concentrations for priority pollutants determined by CLS are all substantially less than the analytical detection limits reported for recent analyses performed using purge-and-trap methods (Table 2).

The compound 2,6-bis-di-tert-butyl-p-benzoquinone (DTBB), an indicator of pollution of water by sewage (Barber et al. 1988), was detected in both samples from well YD-58-50-215 and in one of three samples from well YD-58-42-813. The maximum concentration detected was 30 ng/L from well YD-58-50-215. Coelution of DTBB with the 1-chlorododecane standard may have prevented its detection in some duplicate samples.

The concentrations reported above are semiquantitative because of the lack of recovery data for the reported compounds. Data from CLS-GC/MS analysis of three distilled water samples fortified with 100 ng/L of several compounds provided mean recoveries, referenced to C8Cl, of 85% for PCE, 31% for DTBB, and 25% for ethyl benzene (Barber LB II, written commun. 1987). These results indicate that the concentrations reported in Table 2 need to be considered minimum values.

The chemistry of infiltrating water can be affected by human activities, as indicated by the detection of several synthetic organic compounds in ground water. PCE is used widely in industrial and domestic activities as a degreasing solvent, dry-cleaning fluid, and septic-tank cleaner. Toluene and xylene are common components of gasoline and paint solvents. DTBB is an environmental product of the oxidation of tert-butyl phenol (Lopez-Avila and Hites 1981), a common antioxidant additive.

The degree of sorptive retardation of organic compounds in ground water is an important factor in evaluating a potential tracer of ground-water contamination. Sorptive retardation of organic compounds increases as a function of increasing octanol-water partition coefficient and increased organic carbon content of aquifer solid surfaces (Schwarzenbach et al. 1983). The log octanol-water partition coefficients of compounds detected in this study are 2.29 for TCE, 2.69 for toluene, 2.77 for all xylene isomers, 2.88 for PCE (foregoing values from Callahan et al. 1979) and 4.42 for DTBB (Barber et al. 1988). According to this scheme, and assuming no biotransformation reactions, TCE would be least affected by sorptive retardation and DTBB transport would be relatively more affected by sorptive interactions. Under these conditions, DTBB should be less mobile in ground water and found relatively closer to a contaminant source than the other compounds. The presence and amount of organic carbon on pore surfaces of the freshwater zone of the Edwards aquifer has not been reported in the literature.

The long-term persistence of these organic compounds in the aquifer and their utility as tracers are also a function of their resistance to biotransformation. TCE and PCE have been found to persist in water during batch microcosm and field-infiltration studies conducted under aerobic conditions (Parsons et al. 1985; Schwarzenbach et al. 1983). DTBB would also be expected to resist biotransformation because of its highly branched molecular structure (Barber et al. 1988). Toluene and xylene however, are rapidly degraded under aerobic conditions in batch microcosm and field studies (Wilson et al. 1986). In general, water from the recharge area and parts of the confined zone that contains less than 500 mg/L of dissolved solids also contains greater than 1 mg/L of dissolved oxygen. This indicates the prevalence of aerobic conditions (Buszka 1987), which would favor the resistance of TCE, PCE, and DTBB to biotransformation.

Another source of these compounds can be from atmospheric fallout by precipitation. Concentrations of PCE, toluene, and xylene reported by this study are comparable to or somewhat greater than those in a 1982 sample of rainwater from Los Angeles, California (Kawamura and Kaplan 1983) (Table 2). Analyses of the volatile organic compounds present in local rainfall were not available. Concentrations of these volatile contaminants in recharge to ground water probably would be less than those in rainwater, however, because of (1) sorptive losses onto sediment organic carbon and outgassing from intermittent streams recharging the aquifer, and (2) outgassing during vadose zone flow through the dissolution-modified limestone. Therefore, it is likely that concentrations of PCE, toluene, and xylene in ground water are related to surficial contaminant sources and not to recharge from precipitation.

The detection of PCE in samples from Comal Springs collected 3 weeks apart indicates that extremely small concentrations are persistent in this part of the confined zone. The previous detection of trichlorofluoromethane at concentrations of 5 to 35 ng/L in ground water from the confined zone during 1979 supports this conclusion (Thompson and Hayes 1979). The orifice of Comal Springs sampled during this study derives virtually all its water from the most transmissive part of the confined zone in the San Antonio area (Maclay and Land 1988).

The intermittent detection of compounds other than PCE among single-time replicate samples and variable recoveries of surrogate compounds also may relate to volatilization during sample collection, storage, and transfer. Although sample bottles were sealed with no headspace present, degassing was evident in all sample bottles shortly after collection, particularly those pumped from production wells equipped with turbine pumps. Degassing from the sample would strip volatile organic compounds from the water into the headspace and cause their loss during sample transfer into the CLS sparging vessel. For conditions present during this study, the authors estimate that less than 10% of the respective masses of PCE, toluene, and xylene would be lost by degassing into headspace, on the basis of calculations by Pankow (1986).

In conclusion, two of the compounds detected by this investigation: PCE and DTBB, are potentially viable tracers of human-induced effects on ground-water quality. Results from this reconnaissance indicate a tentative relation between the presence of these compounds and patterns of domestic waste disposal. Other potential sources of these compounds, such as recharge from precipitation or contaminated surface water, need to be evaluated as a part of any future tracer studies.

Acknowledgments. Funding for collection and analysis of the purge-and-trap samples was provided in part by the Edwards Underground Water District, San Antonio, Texas, and the City of Austin, Texas. The authors acknowledge the significant assistance of Peter F. Rogerson, U.S. Geological Survey, Branch of Analytical Services, and Larry F. Land, Paul L. Rettman and Dale L. Pate, Geological Survey, Texas District.

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Received January 2, 1990; accepted March 2, 1990.