

VOCs in Shallow Groundwater in New Residential/Commercial Areas of the United States

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The quality of shallow groundwater in urban areas was investigated by sampling 518 monitoring wells between 1996 and 2002 as part of the National Water-Quality Assessment Program of the U.S. Geological Survey. Well networks were installed primarily in new residential/commercial areas less than about 30 years old (17 studies) and in small towns (2 studies) by randomly locating as many as 30 monitoring wells in each study area. The median well depth was 10 m. Based on samples with age-date information, almost all groundwater was recharged after 1950. Samples were analyzed for 53 volatile organic compounds (VOCs). Concentrations ranged from about 0.001 to 1000 $\mu\text{g/L}$ (median 0.04), with less than 1% of the samples exceeding a Maximum Contamination Level or Drinking Water Advisory established by the U.S. Environmental Protection Agency. Using uncensored concentration data, at least one VOC was detected in 88% of the samples, and at least two VOCs were detected in 69% of the samples. Chloroform, toluene, and perchloroethene were the three most frequently detected VOCs. Dissolved oxygen concentration, estimated recharge index, and land-use were significant variables in logistic regression models that explained the presence of the commonly detected VOCs. Dissolved oxygen concentration was the most important explanatory variable in logistic regression models for 6 of the 14 most frequently detected VOCs. Bromodichloromethane, chloroform, and 1,1,1-trichloroethane had a positive correlation with dissolved oxygen; in contrast, dichloroethane, benzene, and toluene had a negative correlation with dissolved oxygen.

Introduction

The Safe Drinking Water Act Amendments of 1986 and 1996 require each State to implement wellhead protection plans to protect public supply wells from contamination and to investigate existing and potential threats to the quality of public drinking water. The release of volatile organic compounds (VOCs) to air, water, or land can result in contamination of groundwater, although some VOCs also can be formed naturally in groundwater (1). Presently, very little is known about where and under what conditions VOCs can form naturally in groundwater. In urban areas, protecting and preserving groundwater supplies from VOCs can be difficult because of the number of potential sources in homes, commerce, and industry. For example, chloroform is used

as a solvent, is a potential transformation product of other VOCs, and is a disinfection byproduct of drinking water. Detection of low micrograms-per-liter concentrations of VOCs in groundwater may originate, for example, from leaking water mains, lawn irrigation, leaking sewer lines, storm runoff, leaking storage tanks, or even the atmosphere for some VOCs. There could be many potential sources even within a small area.

The fate of VOCs in an aquifer depends on a number of hydrodynamic, abiotic, and biotic processes. Small-scale studies can provide detailed knowledge of the behavior and fate of organic compounds at a particular site for certain geochemical, redox, and hydrogeologic conditions; however, the relevance of this site-specific information needs to be established before it can be applied to other areas. In large-scale resource assessments, knowledge of the behavior and fate of VOCs also can be defined, but this knowledge is based on diverse conditions that are known to occur in large areas.

As part of the National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey (USGS), a plan was developed for urban land-use studies (2) to define shallow groundwater quality in new (generally post-1970) residential/commercial areas in large metropolitan areas and to identify relations between land use and the quality of recently recharged groundwater (generally less than about 10 years old). Residential/commercial areas were targeted for investigation because they comprise the largest land use within metropolitan areas and about 90% of the urban population in the United States lives in metropolitan areas with populations greater than 250,000 (3). New residential/commercial land use in large metropolitan areas was targeted for investigation because these areas often incorporate the latest ideas on urban planning; however, the effect of this new development on groundwater quality is largely unknown. These areas also are of concern because this is where urban growth has occurred most rapidly in the United States. Small towns are important because they are frequently dependent on groundwater as a water supply and little was known about the effect of land use on the shallow groundwater quality.

The purpose and scope of this paper are (i) to summarize the occurrence, distribution, and status of VOCs in shallow groundwater in new residential/commercial areas, and to much lesser extent small towns, in the United States, 1996–2002, and (ii) to examine some variables that may be associated with the source, transport, and fate of the most frequently detected VOCs.

Methods

Sampling Program. Seventeen urban land-use studies were located near cities with populations much greater than 250,000, and two studies in Iowa/Minnesota and Colorado were focused on small towns (Figure 1, Table 1). In small towns, new residential/commercial areas were not specifically targeted because of the small amount of this type of development.

The metropolitan areas for the urban land-use studies were selected on the basis of geographic distribution, groundwater use, hydrogeologic conditions, and amount of new residential/commercial area. Sites were geographically distributed across the United States. Urban land-use studies were located in areas where shallow groundwater was used as a water supply or where it was hydraulically connected to deeper groundwater used as a supply. There may have been multiple sources of water in an area and groundwater may not have been the dominant source of water, but new residential/commercial developments generally were more

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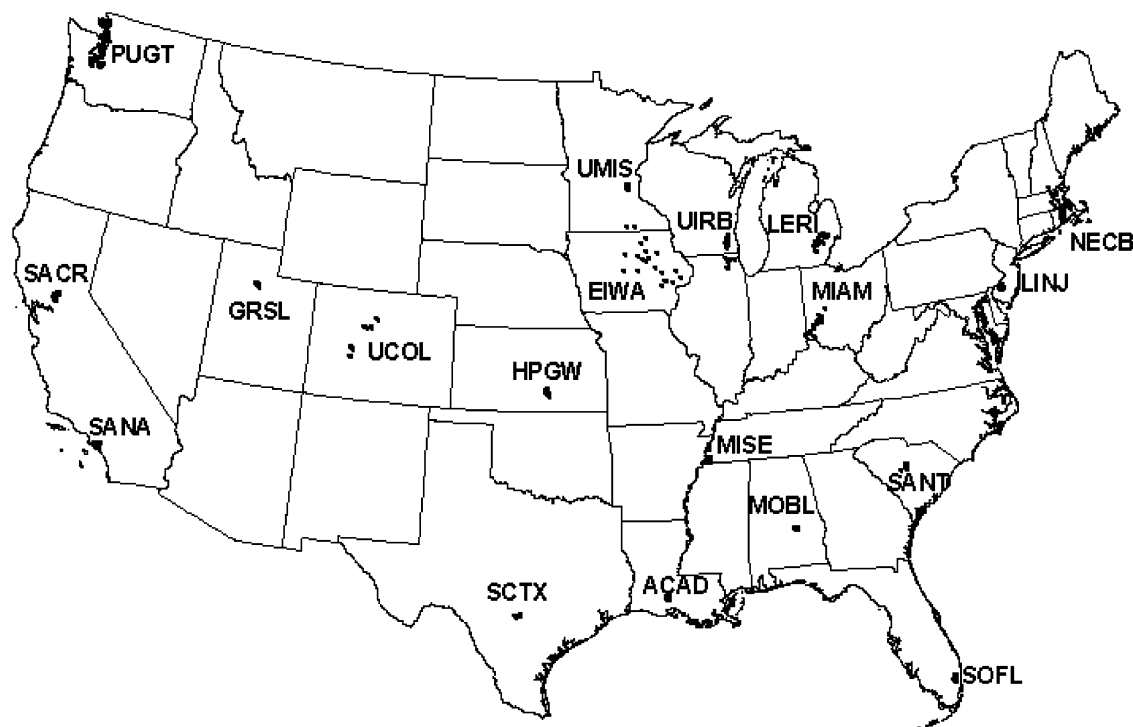


FIGURE 1. Well locations within 19 urban land-use study areas (identified using abbreviations in Table 1).

TABLE 1. Location, Number of Wells, and Hydrogeologic Information for Each Urban Land Use Study

study unit	location	no. of wells	principal aquifer	lithology	median depth to water (m)
ACAD	Lafayette, Louisiana	27	Coastal Lowlands	sand, some silt, clay	12.80
EIWA	small cities in Iowa	30	Glacial deposits	sand, gravel, silt, clay	3.33
GRSL	Salt Lake City, Utah	29	Basin and Range	sand, gravel, some clay, silt	17.81
HPGW	Wichita, Kansas	30	Alluvial	sand, gravel, clay, some silt	4.91
LERI	Detroit, Michigan	30	Glacial	sand, gravel, some clay	3.86
LINJ	Glassboro, New Jersey	30	North Atlantic Coastal Plain	sand, some clay, silt	3.66
MIAM	Dayton/Cincinnati, Ohio	25	Glacial deposits	sand, gravel, clay, silt	7.36
MISE	Memphis, Tennessee	29	Surficial aquifer, Mississippi Embayment, Texas Coastal Uplands	sand, gravel, silt, clay	10.41
MOBL	Montgomery, Alabama	30	Southeastern Coastal Plain	sand, gravel	7.57
NECB	Boston, Massachusetts	28	Glacial deposits	sand, some gravel, silt	3.73
PUGT	Tacoma, Washington	27	Glacial deposits	sand, gravel, clay, silt	9.33
SACR	Sacramento, California	19	Central Valley Aquifer	sand, gravel, silt, clay	7.12
SANA	Orange County, California	26	California Coastal basin	sand, clay, silt	2.48
SANT	Columbia, South Carolina	29	Southeastern Coastal Plain	clay, some sand	3.09
SCTX	San Antonio, Texas	30	Edwards-Trinity	limestone, dolomite	57.74
SOFL	Fort Lauderdale/Miami, Florida	27	Biscayne	limestone	1.42
UCOL	small cities in Southern Rocky Mts, Colorado	24	Alluvial	sand, gravel, silt, clay	2.88
UIRB	Chicago, Illinois and Waukesha, Wisconsin	19	Glacial deposits	sand, cobbles, silt, clay	3.84
UMIS	Minneapolis, Minnesota	29	Glacial deposits	sand, gravel, silt, clay	3.98
		total 518			

dependent on groundwater than was the metropolitan center. A variety of hydrogeologic conditions and principal aquifers (Table 1) were represented by the selected locations for urban land-use studies representing varying depths to water (Table 1), permeability of unsaturated zones, and the amount of groundwater recharge. Urban land-use studies were selected only in areas that contained sufficient new residential/commercial development to accommodate the preferred network of 30 monitoring wells.

The 518 monitoring wells sampled in the urban land-use studies were installed by the USGS using procedures described by Koterba et al. (4). Well locations were randomly distributed within the study areas, and a minimum well

spacing of about 1 km was maintained to reduce the risk of autocorrelation for land-use analysis. For each study, as many as 30 wells were installed. No glue was used in the 2-in. poly(vinyl chloride) well casings. Auger rigs were used for well installation in most studies.

The sampling plan (4) allowed for groundwater age estimates to be based on a variety of dating methods that included identification and quantitation of chlorofluorocarbons, tritium, tritium/helium ratios, and sulfur hexafluoride. Staff responsible for each urban land-use study decided which age-dating method to use, but the decision generally was based on financial considerations. Although different hydrogeologic conditions were investigated, it was expected

that most recharge water reached the water table within 10 years and that the water chemistry at the top of the water table reflects land-use activity and attenuation properties of the unsaturated zone. On the basis of estimated age dates for 139 samples, the water was recharged after 1950 for 95% of the samples. Consequently, almost all groundwater sampled was recently recharged water even though the exact year of recharge was not always determined because of limitations of the age-dating techniques. Among the 104 samples with an actual year associated with the age-date, the median age was about 10 years.

The wells were installed in shallow groundwater and screened near the top of the water table; the median well depth was 10 m with a median screened interval located 4 m below the water table. In San Antonio, Texas (SCTX, Figure 1), however, the wells were much deeper with a median depth of 80 m and a median screened interval located 23 m below the water table. The deeper screens were installed to accommodate groundwater fluctuations in the karst topography of the Edwards–Trinity aquifer.

Sampling Methods. All wells were sampled according to procedures described by Koterba et al. (4). VOC samples were collected in 40-mL amber glass vials using Teflon tubes to fill each vial from the base until overflow occurred. Samples were stored on ice or refrigerated until analysis. One sample per well was used for the analyses in this report.

Samples were analyzed for 53 halogenated and nonhalogenated VOCs at the USGS National Water Quality Laboratory in Denver, Colorado. These VOCs were identified as part of the target analytes selected by the VOC National Synthesis Team of NAWQA (5). Bender et al. (5) documented the major uses, chemical formulas, and molecular weights for each of these 53 VOCs. The method of analysis used was purge-and-trap, capillary column gas chromatography/mass spectrometry as described by Connor et al. (6). Some of the smallest reported concentrations were estimated, indicating quantitative uncertainty. Identification was confirmed by gas chromatographic retention time and by the resultant mass spectrum typically identified by three unique ions (6). The concentration level for identification and quantification varied by VOCs. Uncensored data provide the lowest detection levels and concentration values for each VOC. These data are appropriate for some analyses, but should not be used to make comparisons between VOCs because of differences in analytical capability between VOCs. A common censoring level at a concentration at which all VOCs can be reliably identified and quantified, for example 0.1 or 0.2 $\mu\text{g/L}$, is necessary to make comparisons between VOCs.

Source solution blanks, equipment blanks, field blanks, laboratory blanks, replicate samples, and spike samples are some of the types of quality-control/-assurance samples that were collected on a routine basis. The results of the field blank samples were reviewed to identify systematic contamination due to the sampling procedures. There were only four samples that had possible systematic contamination of MTBE; these MTBE analyses were dropped from the data set.

Statistical Methods. Quantile plots were used to show the distribution of the sample data. The quantile of a sample is the data point corresponding to a given fraction of the data at or less than an indicated concentration (7). A quantile plot looks like a cumulative sample distribution function. The spread, skewness, and other characteristics of all the data could be examined in these plots; furthermore, more of the data can be displayed in this manner than in boxplots. The quantile distributions plots shown in this paper start at the fraction of data with a detected concentration. Direct comparisons between concentration distributions in two data sets also were displayed by graphing the quantiles of one data set against the second in quantile/quantile plots (7).

An alpha level of 0.05 was used for all statistical analyses that included contingency tables, Wilcoxon rank-sum test, Wilcoxon signed-rank test, Kolmogorov–Smirnov, Spearman's rho, Pearson's r, Wald's t, Akaike's Information Criteria, McFadden's rho-squared, Hosmer/Lemeshow statistic, and log likelihood. These statistics are described in statistical books, for example, Menard (8) and Helsel and Hirsch (7). Contingency tables were used to measure the association between two nominal categorical variables if the populations of all cells were greater than or equal to five. The Wilcoxon rank-sum test was used to test difference between two nominal categorical variables if a contingency table could not be used because one or more cells had a population of less than five. The Wilcoxon signed-rank test was used to test whether matched paired values in one group were larger than those in a second group. Kolmogorov–Smirnov and Wilcoxon rank-sum tests are nonparametric tests that can be used to determine if the distributions of two data sets are different. Spearman's rho was calculated to determine correlations between ranked concentrations in two data sets. Pearson's r was calculated to measure the linear correlation between two data sets. Wald's t, Akaike's Information Criteria, McFadden's rho-squared, Hosmer/Lemeshow statistic, and log likelihood are all statistics used to evaluate logistic regression models.

Logistic regression models were used to show associations of multiple explanatory variables (independent variables) with the presence/absence of a particular VOC (dependent variable). Logistic regression models transform the estimated probabilities into a continuous response variable. The transformed response is subsequently retransformed back to a value between 0 and 1. The explanatory variables can be continuous or binary. The results of these models only show associations and were not developed to be predictive models. For logistic regression models, unstandardized coefficients were recalculated in standard deviation units so that the magnitude of the standardized coefficients could be directly compared (8). A standardized coefficient indicated how many standard deviations of change in the dependent variable were associated with a 1-standard-deviation increase in the independent variable as follows:

$$b_{YX}^* = (b_{XY})(s_X)(R)/s_{\logit(\hat{Y})}$$

where b_{YX}^* is the standardized logistic regression coefficient, b_{XY} is the unstandardized logistic regression coefficient, s_X is the standard deviation of the independent variable X , R is the correlation coefficient, and $s_{\logit(\hat{Y})}$ is the standard deviation of the $\logit(\hat{Y})$, where $\logit(\hat{Y})$ is the natural logarithm of the odds ratio.

Logistic regression models were used to look for associations between shallow groundwater quality at a particular location and current land-use activity within a circular buffer with a 500-m radius around the sampling point. No groundwater flow analysis was done to document the source of water to the monitoring well. A number of possible conditions may exist that could adversely affect the results of this analysis including: available land-use data are not sufficiently accurate, prior land-use activity affects water quality, current land-use activity has not had time to affect shallow groundwater, anthropogenic activity outside the 500-m buffer affects groundwater quality, only small areas within the 500-m buffer affect water quality, and point source contamination could be sufficiently dispersed to give the appearance of nonpoint source contamination. Despite these potential problems, a number of previous studies have shown a relation between land use and water quality (9–13).

For each VOC, a number of logistic regression models are possible, but information from a variety of statistical measures (log likelihood, Wald's t, Akaike's Information Criteria,

McFadden's rho-squared, and Hosmer/Lemeshow statistic (7, 8)) were used to select the final model. These models all had explanatory variables with a Wald's t p -value of < 0.05 . The log likelihood was minimized, and nonnested models were compared using the Akaike's Information Criteria. Models with a large McFadden's rho-squared were selected over those with lower values, and when possible models with a high Hosmer/Lemeshow statistic were selected over those with lower values to ensure that the model was not unduly affected by a small number of unusual observations. Although a variety of statistical measures were used to evaluate the many possible models, these models should not be viewed as definitive. These models may change as more detailed ancillary or groundwater flow information becomes available; nevertheless, some general conclusions can be drawn from the results of these initial models.

Ancillary Data. Ancillary information used for the logistic regression models was compiled from existing data and collected by USGS personnel. Land-use characteristics within 500 m of the sampled well were derived from aerial photographs, and were field checked and documented using procedures described by Koterba (14). Urban land-use characteristics included surface water, single-family housing, multi-family housing, park, vacant, commercial, industrial, transportation, and forest. Hydrogeologic information like well depth, water levels, and type of aquifer was collected by the USGS.

Data from the U.S. Bureau of Census (3), STARVIEW (15), and U.S. Environmental Protection Agency (USEPA) (16) also were used in the analysis. Census block data from the 1990 U.S. Bureau of the Census (3) were used to calculate the median age of homes, population density, and density of homes on septic systems, public water systems, and public sewer systems. STARVIEW (15) data were used to calculate the densities of underground storage tanks and leaking underground storage tanks (LUST) around the sampled wells. For each 500-m-grid cell, the density of underground and leaking gasoline tanks was calculated using a 1000-m circular buffer. A larger circular buffer was used because of the uncertainty associated with the locations of some of the tanks. The gasoline tanks were distinguished from sources such as dry cleaners and other tanks by looking for a number of key words in the name of the business that would identify gasoline stations and dry cleaners. Data from USEPA (16) and TRW Petroleum Technologies (17) were used to define areas that used methyl *tert*-butyl ether (MTBE) in gasoline at concentrations greater than 3 vol %.

Groundwater recharge is an important explanatory variable because of its potential to quickly transport VOCs to the water table. Areas with large recharge can have less residence time for degradation/transformation to occur within the unsaturated zone. Wolock (18) estimated groundwater recharge indices for the United States using 8249 USGS streamgages with at least 10 years of record. This method assumes (i) steady-state conditions, implying that recharge was equal to groundwater discharge; (ii) recharge was discharged to streams, and (iii) groundwater discharge to streams could be estimated by multiplying a base-flow index (BFI) times long-term mean annual runoff. Streamgages on large river systems in the United States were not included in this analysis; consequently, the recharge estimates were representative of the local and possibly intermediate groundwater flow system. Recharge to the deep regional groundwater flow system probably was not reflected in the recharge estimate. The BFI was calculated at each streamgage using the Wahl and Wahl (19) hydrograph separation technique. A grid was created from the BFI values using an inverse distance-weighting method. This grid was multiplied by a grid of mean annual runoff (20) to generate the mean annual recharge value for the conterminous United States and to

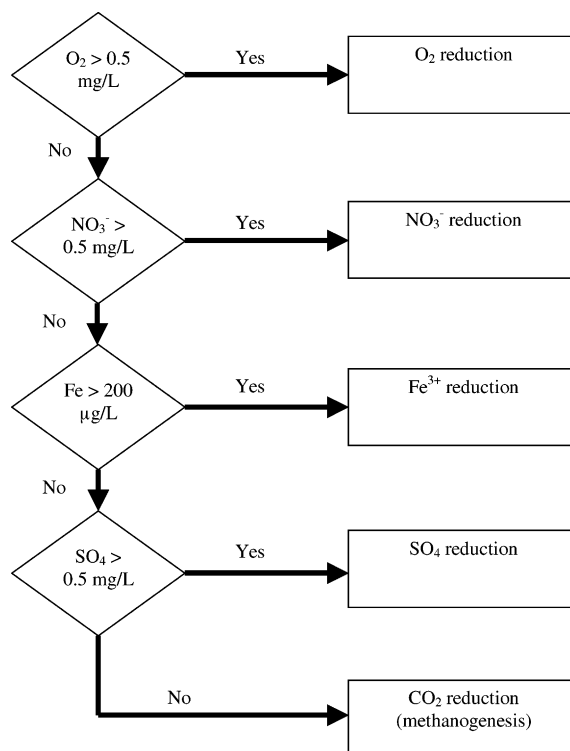


FIGURE 2. Simplified hierarchical scheme for estimating predominant redox condition.

provide point recharge estimates for the urban land-use study wells.

Irrigation may augment the transport of VOCs with groundwater recharge. The amount of irrigation during the summer months varied substantially among the study areas. On the basis of water-use information collected from the water suppliers and the size of the metropolitan area, irrigation in six metropolitan areas varied from 0.005 to 1.5 mm/d (irrigation information for the other areas was not available). It is not known how much of this water applied to the land surface actually recharged the shallow groundwater. Evapotranspiration was largest during the summer months when irrigation occurred; nevertheless, any irrigation return flow to the groundwater should be reflected in the recharge index estimate. Although Wolock's recharge estimate (18) has limitations, this probably is the best recharge estimate currently available at a national scale for local and possibly intermediate groundwater flow systems.

Redox Classification. Concentrations of oxygen, nitrate, iron, and sulfate were used to estimate the predominant redox condition (Figure 2). Flow-through chambers were used for collection of dissolved oxygen (4). Field meters were sufficient for most dissolved oxygen measurements, but spectrophotometric or iodometric methods were necessary for accurate measurements of dissolved oxygen at concentrations less than 1 mg/L. Major ions and trace elements were analyzed by using atomic absorption spectrometry (21). Dissolved total iron is reported. Nitrate analysis is described by Fishman (21) and Patton and Truitt (22). Nitrite-plus-nitrate concentrations are based on elemental nitrogen (e.g., NO_2^- plus NO_3^- as N) and are referred to in this paper as "nitrate" because the nitrite contribution generally is negligible in groundwater.

A hierarchical scheme is simplified from that presented by Chapelle et al. (23) because there were no measurements of hydrogen and methane for the samples or concentration measurements along the direction of groundwater flow—all necessary measurements for definitive identification of redox. On the basis of this simplified scheme, 374 samples were

TABLE 2. Most Frequently Detected VOCs in the Current Investigation Compared With Previous Investigations

compound	abbreviation	detection frequency (%)			detection frequency (%)	
		uncensored	current investigation		censored at 0.2 µg/L	
			censored at 0.1 µg/L	censored at 0.2 µg/L	urban wells (various well types), ref 24	primarily rural drinking water wells (untreated), ref 25
ethylbenzene		9.3	0.4	0.4	1.7	0.1
chloromethane		13.0	1.2	0.8	1.1	0
<i>o</i> -xylene		6.0	0.8	0.8		
1,1-dichloroethane	(1,1-DCA)	6.9	2.1	1.0	6.4	0.4
benzene		11.2	1.7	1.0	3.5[0.1]	0.3
1,2,4-trimethylbenzene	(TMB)	12.5	1.4	1.2	1.7	0.5
<i>m</i> - and <i>p</i> -xylenes		14.3	2.3	1.2		
xylenes (<i>o</i> -, <i>m</i> -, and <i>p</i> - xylenes)		15.0	2.3	1.4	2.2	0.3
bromodichloromethane		14.1	3.9	1.7	3.0	0.8
trichloroethene	(TCE)	8.3	2.3	1.7	11.6[1.2]	1.5 [0.1]
1,1,1-trichloroethane	(TCA)	23.2	4.6	3.1	9.7	1.5
toluene		35.5	6.0	3.1	3.3	1.1
perchloroethene	(PCE)	28.1	6.0	3.9	16.6[3.4]	2.9 [0.2]
methyl <i>tert</i> -butyl ether	(MTBE)	13.7	9.5	7.3	16.9	3.7
chloroform		48.1	19.3	13.9	26.4[0.2]	7.3

TABLE 3. Compounds Exceeding Maximum Contaminant Level (MCL) or Drinking Water Advisory (DWA) in Samples

compound	concn. (µg/L)	MCL/ DWA	no. exceeding	no. of analyses	percent exceeding	study area abbreviations (no. exceeding)
benzene	5	MCL	2	518	0.4	EIWA(2)
chloroethene	2	MCL	1	518	0.2	EIWA(1)
1,2-dichloroethane	5	MCL	1	518	0.2	EIWA(1)
PCE	5	MCL	3	513	0.6	MOBL(1), HPGW(1), GRSL(1)
MTBE	20–40	DWA	4	518	0.8	EIWA(2), NECB(1), SANT(1)

oxic, 37 samples were nitrate reducing, 70 samples were iron reducing, 34 samples were sulfate reducing, and only 3 samples were methanogenic (not considered in further analysis).

Results

Occurrence, Distribution, and Status. The occurrence of VOCs is summarized and listed in the Supporting Information (Tables A1–A3). VOCs were frequently detected; in fact, 88% of the samples had at least one VOC (using uncensored concentration data). The 14 most frequently detected VOCs and their abbreviations are listed with detection frequencies in Table 2. These VOCs were not distributed within just a few urban land-use studies; in fact, these 14 VOCs were among the most frequently detected VOCs in all the urban land-use studies.

The 14 most frequently detected VOCs had detection frequencies greater than 5% on the basis of uncensored concentration data. A comparison of VOC detection frequencies using uncensored data may be misleading because analytical capabilities vary among VOCs; however, the data were uniformly censored at 0.1 µg/L so that comparisons could be made (Table 2). This censoring changed the rank order of the most frequently detected VOCs, but the most notable was MTBE, which increased in ranked detection frequency from seventh to second. Concentrations of MTBE generally are larger than those of other VOCs, with the exception of chloroform.

VOC detection frequencies for this current investigation were compared to those of previous investigations (Table 2). Squillace et al. (24) reported VOC data from 406 wells (including a variety of well types) in a variety of urban areas across the United States. In another study, Squillace et al. (25) reported VOC data from untreated samples from 1497 drinking-water wells sampled across the United States, but

only 120 of these wells were located in urban areas. The data were censored at 0.2 µg/L, so that detection frequencies could be compared directly (Table 2). Among the 13 VOCs compared (*m*- and *p*-xylenes and *o*-xylene were combined), detection frequencies in the current investigation were significantly smaller compared to those of groundwater samples from other urban land-use areas (24), but significantly larger than samples from rural drinking-water wells (25) according to the Wilcoxon signed rank test. Chloroform, PCE, MTBE, TCA, TCE, and 1,1-DCA had detection frequencies at least 5% greater in other urban land-use areas compared to the current investigation. More frequent detections of solvents in these urban wells may be associated with industrial activity that was intentionally avoided in the current investigation. Chloroform, MTBE, and toluene had a detection frequency of at least 2% more for the current investigation compared to rural areas. These three VOCs represent a mix of possible sources including disinfection byproduct, gasoline, and solvents.

The status of VOCs in shallow urban groundwater was determined by comparing measured concentrations to maximum contaminant levels (MCL) or drinking water advisories (DWA) established by the USEPA. Table 3 shows that five compounds (benzene, chloroethene, 1,2-dichloroethane, PCE, and MTBE) exceeded an MCL or DWA established by the USEPA, but in less than 1% of the samples for each of these five VOCs.

At least 90% of all concentrations were less than 1 µg/L. Concentrations ranged from about 0.001 to 1000 µg/L (median 0.04 µg/L). The top three most frequently detected halogenated and nonhalogenated VOCs (uncensored concentrations) were those with the largest concentrations (Figure 3). The nonparametric Kolmogorov–Smirnov test was used to compare the cumulative distributions of the VOC concentrations. VOCs that were not different were

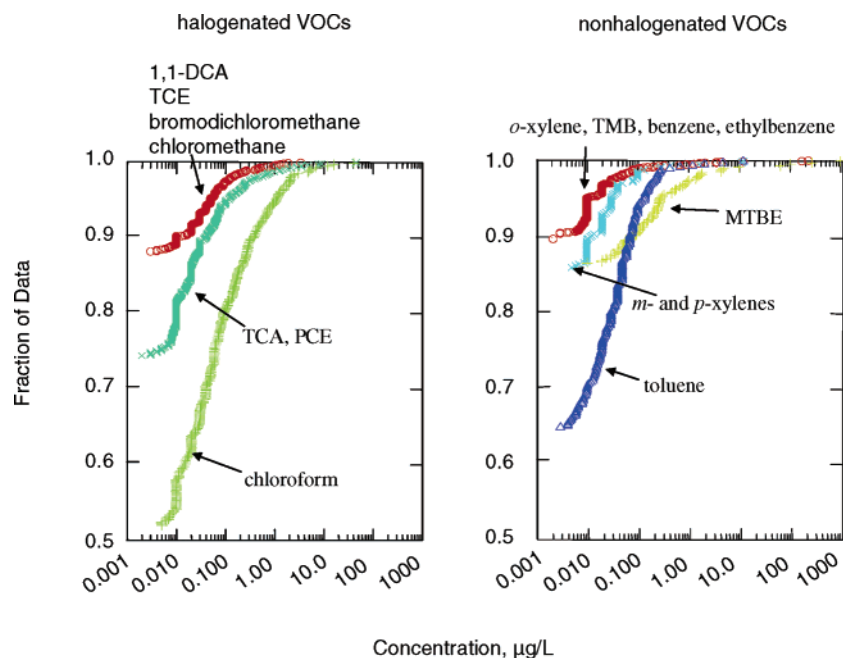


FIGURE 3. Quantile plots showing concentrations of the 14 most frequently detected VOCs.

combined; consequently, all quantile profiles shown in Figure 3 are significantly different. The actual composition of gasoline varies; however, concentrations of toluene, *m*- and *p*-xylenes, and MTBE in gasoline are among the largest in gasoline (26) and had the largest concentrations in ground-water compared to other nonhalogenated VOCs (Figure 3). Chloroform, PCE, and TCA had the largest concentrations among the halogenated VOCs.

Multiple VOCs were commonly found together in a single sample; in fact, 69% of the samples had at least two VOCs. The frequent detection of two or more VOCs in samples raises the question of whether there are significant correlations between concentrations of certain pairs of VOCs. Table 4 A and B show a matrix of Spearman's rank-order correlation coefficients for the halogenated and nonhalogenated VOCs. Coefficients that are statistically significant are shown in bold. For example, the Spearman's correlation coefficient of the rank ordered concentrations of bromodichloromethane with chloroform was 0.60 and was statistically significant. Among the halogenated VOCs, 12 of 21 possible paired combinations were significantly correlated using the Spearman's correlation. Chloromethane was not significantly correlated with any of the other six halogenated VOCs. Among the nonhalogenated VOCs, 13 out of 21 possible paired combinations were significant. MTBE was not correlated with any of the other six nonhalogenated VOCs. In summary, VOC concentrations within the halogenated and nonhalogenated VOCs groups generally were correlated with the exception of chloromethane and MTBE.

There were only a few halogenated VOCs that had concentrations that were significantly correlated with nonhalogenated VOCs. In fact, a Spearman's correlation matrix comparing ranked ordered concentrations of paired halogenated versus nonhalogenated VOCs showed that only 4 of 49 possible paired combinations had a positive significant correlation (Table 4C) indicating little association of VOC concentrations between these two groups of VOCs. The significant correlations were between MTBE and chloroform, PCE, and 1,1-DCA, and between benzene and chloromethane. The strongest correlation was between MTBE and 1,1-DCA (0.28); the remaining correlation coefficients were less than 0.2.

The seven nonhalogenated VOCs listed in Table 2 are commonly found in gasoline, which is a vast potential source

of these VOCs. MTBE is not found in all gasoline but is commonly used as an octane enhancer and as a fuel oxygenate. The seven halogenated VOCs listed in Table 2 do not share a single common source, and, yet, halogenated VOCs were about twice as likely to be found together (mixture) with other halogenated VOCs compared to nonhalogenated VOCs. In fact, among samples with mixtures, 64% had mixtures of halogenated VOCs compared with 34% with mixtures of nonhalogenated VOCs if chloromethane and MTBE are excluded. These two VOCs were not associated with the other VOCs within their group (Table 4). There are many possible reasons why halogenated VOCs were more frequently detected in mixtures compared with nonhalogenated VOCs. For example, halogenated VOCs may be more persistent than nonhalogenated VOCs (27, 28) in the normally oxic water, halogenated parent and transformation products were analyzed, but transformation products of nonhalogenated VOCs were not part of the 53 VOCs analyzed for this investigation, and some industrial products may contain mixtures of halogenated VOCs.

Electron Acceptor Status. The following three sections show the importance of redox/dissolved oxygen concentration, recharge, and land use on the detection and concentrations of VOCs. The effect of strong explanatory variables can sometimes be established using univariate analysis; however, the effect of other variables may not be evident unless multivariate analysis is used. In multivariate analysis, one controls for the effect of one variable while testing explanatory power for other variables. Consequently, in this paper univariate analysis on redox is followed by bivariate analysis for redox and recharge, which in turn is followed by multivariate logistic regression analysis. Each section becomes more inclusive in the variables tested.

The fate of VOCs in shallow groundwater of urban areas is controlled in large part by redox conditions; in fact, dissolved oxygen concentration was the most important explanatory variable in logistic regression models developed for the 14 most frequently detected VOCs (discussed in a subsequent section). Although there were only 144 samples with anoxic water, analyses also were done to look at the effect of specific redox conditions on occurrence and concentrations of VOCs.

Analysis of detection frequencies of selected parent compounds and some potential transformation products

TABLE 4. Spearman's Correlations for VOC Concentrations, Estimated Recharge Index, and Dissolved Oxygen^a

(A) Halogenated VOCs								
	chloroform	bromodichloromethane	PCE	TCE	TCA	1,1-DCA	chloromethane	recharge index
bromodichloromethane	0.60							
PCE	0.33	0.30						
TCE	0.11	0.18	0.33					
TCA	0.39	0.31	0.22	0.19				
1,1-DCA	0.00	-0.02	0.21	0.32	0.23			
chloromethane	0.00	0.00	-0.01	0.06	-0.04	0.06		
recharge index	0.06	-0.15	-0.14	-0.04	0.16	0.07	0.12	
dissolved oxygen	0.49	0.28	0.20	0.00	0.30	-0.15	-0.04	0.15

(B) Nonhalogenated VOCs								
	toluene	benzene	ethylbenzene	TMB	<i>o</i> -xylene	<i>m</i> - and <i>p</i> -xylenes	MTBE	recharge index
benzene	0.18							
ethylbenzene	0.32	0.21						
TMB	0.11	0.24	0.22					
<i>o</i> -xylene	0.25	0.13	0.67	0.19				
<i>m</i> - and <i>p</i> -xylenes	0.31	0.24	0.75	0.26	0.64			
MTBE	0.02	0.14	-0.06	-0.04	-0.02	-0.07		
recharge index	0.05	0.10	0.15	0.12	0.15	0.17	0.21	
dissolved oxygen	-0.18	-0.12	-0.05	-0.09	-0.03	-0.07	0.03	0.15

(C) Halogenated versus Nonhalogenated VOCs								
nonhalogenated VOCs	halogenated VOCs							
	chloroform	bromodichloromethane	PCE	TCE	TCA	1,1-DCA	chloromethane	
toluene	-0.20	-0.14	0.00	-0.01	-0.04	0.03	-0.04	
benzene	-0.13	-0.09	0.00	0.06	-0.04	0.13	0.19	
ethylbenzene	-0.13	-0.09	-0.04	-0.10	-0.01	-0.09	-0.02	
TMB	-0.08	-0.08	-0.04	-0.07	-0.11	-0.03	0.04	
<i>o</i> -xylene	-0.09	-0.08	-0.04	-0.05	0.06	-0.04	-0.06	
<i>m</i> - and <i>p</i> -xylenes	-0.14	-0.09	-0.07	-0.07	-0.02	-0.07	-0.07	
MTBE	0.18	0.03	0.18	0.15	0.15	0.28	0.08	

^a Bold correlations are significant at 0.05 alpha level.

shows the importance of redox for compound stability and formation of potential transformation products. The detection frequencies (number of uncensored detections divided by the number of samples) were calculated for chloroform, PCE, toluene, and benzene in Figure 4A for oxic, nitrate reducing, iron reducing, and sulfate reducing conditions. Detection frequency of chloroform and PCE generally decreased with more reducing conditions (Figure 4A). Detection frequencies of toluene and benzene do not follow a clear trend with more reducing conditions (Figure 4A); however, the detection frequencies in oxic conditions are significantly lower than those in anoxic conditions (nitrate, iron, and sulfate reducing conditions combined) for these two VOCs. The detection frequencies of four potentially important transformation products (chloroethane, vinyl chloride, *cis*-1,2-dichloroethene (*cis*-1,2-DCE), and 1,1 dichloroethane (1,1-DCA) for oxic and anoxic conditions are shown in Figure 4B. The detection frequencies between oxic and anoxic conditions for these four VOCs are significantly different. Detection frequency of four potential transformation products increased by a factor of 2 to more than 10 times in anoxic water compared to oxic water: chloroethane (7 times), vinyl chloride (12 times), *cis*-1,2-DCE (6 times), and 1,1-DCA (2 times) (Figure 4B).

Spearman's correlations between individual VOC concentrations and dissolved oxygen (Table 4A and B) showed that five halogenated VOCs and one nonhalogenated VOC were correlated with dissolved oxygen concentration. Halogenated VOC concentrations had a positive correlation with dissolved oxygen indicating greater stability in more oxic conditions, with the exception of 1,1-DCA, which is probably

a transformation product of TCA in anoxic water. Chloroform concentrations were most strongly correlated with dissolved oxygen. The concentrations of toluene had a negative correlation with dissolved oxygen indicating greater stability in less oxic conditions; this relation also has been established in previous investigations (27, 28). All the remaining nonhalogenated VOCs were negatively correlated with dissolved oxygen concentrations but the strength of these correlations was not statistically significant.

The concentrations of toluene and chloroform are affected by redox conditions in a manner that is consistent with previous investigations. A comparison of the concentrations of these two VOCs in different redox conditions is interesting because they are frequently detected and have contradictory stabilities in the presence of oxygen. The Spearman's correlations (Table 4A and B) showed that chloroform concentrations increase with larger concentrations of oxygen; in contrast, toluene concentrations increase with decreasing concentrations of oxygen. A quantile/quantile plot (Figure 5) shows how the concentrations of chloroform and toluene, relative to each other, varied with redox condition. Under oxic conditions, chloroform concentrations were larger as was expected because chloroform should be more stable under oxic conditions compared to toluene (27). Under nitrate-reducing conditions, the concentrations were about equal and may represent a transition between oxic and more reducing conditions. Under iron-reducing conditions, toluene concentrations were larger than chloroform concentrations as was expected because toluene should be more stable under this anoxic condition (27). Under sulfate-reducing conditions, the concentrations of toluene were still larger

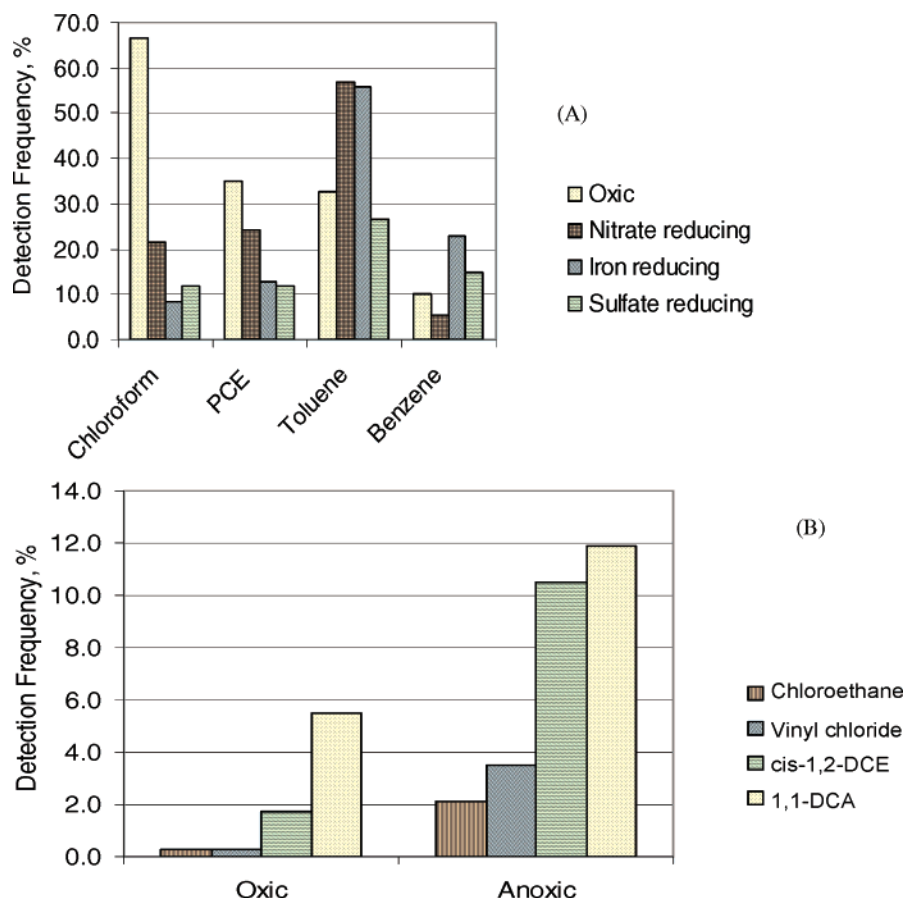


FIGURE 4. Effect of redox on detection frequency of selected parent compounds (A) and some potentially important transformation products (B).

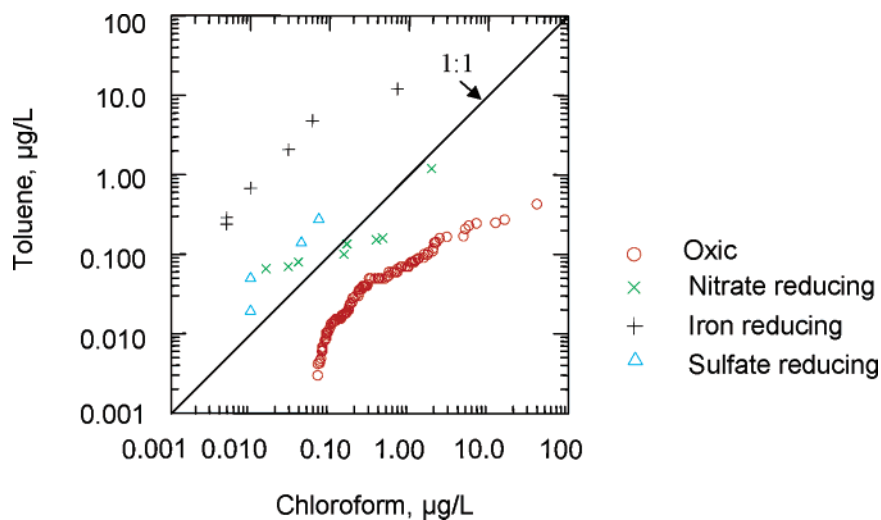


FIGURE 5. Quantile/quantile plot showing the relation of chloroform and toluene concentrations under redox conditions.

than chloroform concentrations but were less than under iron-reducing conditions. Perhaps degradation of toluene occurred more quickly under sulfate-reducing conditions than under iron-reducing conditions, which is supported by previous investigations (28). The concentrations of other VOCs also could be affected by redox conditions, but the frequent detections of chloroform and toluene provided sufficient concentration data for this analysis.

Dissolved Oxygen Availability and Recharge. The concentrations of five VOCs had a positive significant correlation with estimated groundwater recharge (Table 4A and B), indicating the importance of recharge as a transport variable

for some VOCs. More nonhalogenated VOCs (four) had a positive correlation with recharge than halogenated VOCs (one). These differences may be related to the sources of the VOCs and recharge water. Anthropogenic activities can increase recharge; for example, irrigation, infiltration basins, recharge wells, septic systems, and leakage from water and sewer lines. Some of these activities can be the source of some VOCs detected in shallow groundwater.

Recharge and dissolved oxygen represent significant transport and fate variables for some VOCs; consequently, these variables also were used to identify similarities and differences between urban land-use studies. The median

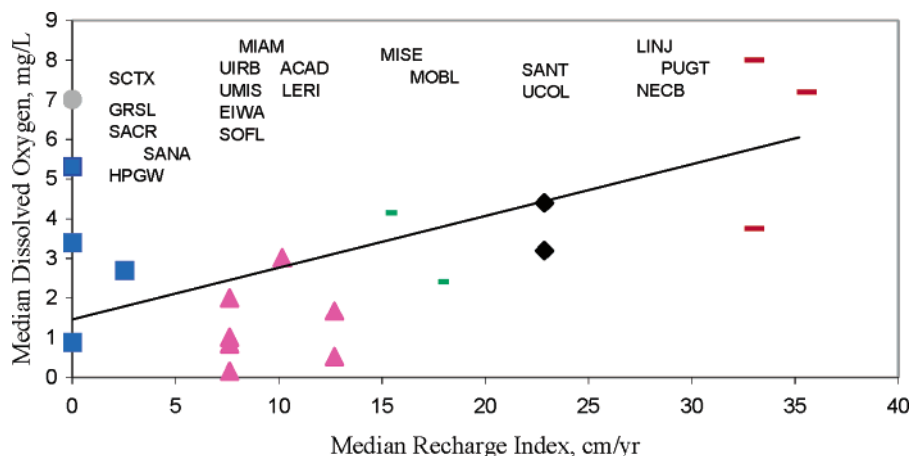


FIGURE 6. Relation between estimated recharge index and dissolved oxygen by land-use study areas (identified using abbreviations in Table 1 and Figure 1). The different symbols used to identify land-use studies indicate the six cluster groups identified by single linkage and Euclidean distances of recharge and dissolved oxygen.

recharge index and median dissolved oxygen concentration for each urban land-use study are shown in Figure 6. The Pearson's linear correlation coefficient between these two variables ($r = 0.61$) was statistically significant ($p < 0.05$) if data from the urban land-use study in San Antonio, Texas (SCTX, Figure 1) were not considered in the regression; the SCTX urban land-use study was unique because it sampled a karst aquifer system (Edwards-Trinity aquifer). Rapid recharge in karst systems does not allow time for microbial utilization of oxygen before reaching the shallow groundwater. Recharge estimates of zero, generated by Wolock (18), occur in areas where there is little base flow, and for some areas (for example, SCTX and GRSL) this estimate is too low. If better estimates were available in these arid regions, the correlation between recharge and dissolved oxygen would probably improve.

The 19 urban land-use studies fell into six groups as shown in Figure 6. The basis of these groups was cluster analysis of recharge and dissolved oxygen using single linkage and Euclidean distances. There appear to be some similarities in the groups of studies. Coastal studies grouped together (LINJ, PUGT, and NECB) as did humid Midwest and Southeastern coastal studies (UIRB, UMIS, EIWA, SOFL, MIAM, ACAD, and LERI). Humid Southeastern SANT and mountainous UCOL studies grouped together. The Humid Southeastern MISE and MOBL studies grouped together. Dry climates, primarily in the Southwest, characterized the GRSL, SACR, HPGW, and SANA group. SCTX was unique because of the karst system investigated.

Dissolved Oxygen Availability, Recharge, and Land Use.

Dissolved oxygen concentration, estimated recharge index, and land-use activity were the most important variables that explained the presence of VOCs according to the results of the logistic regression analysis (Table 5). Dissolved oxygen concentration was the most important explanatory variable for 6 of the 14 VOCs as indicated by the standardized coefficients, and was a significant explanatory variable for an additional 3 VOCs (Table 5). Four halogenated VOCs (chloroform, PCE, TCA, and bromodichloromethane) had a positive correlation with dissolved oxygen indicating greater stability in oxic condition; but 1,1-DCA had a negative correlation with dissolved oxygen. 1,1-DCA probably is a transformation product of TCA in anoxic conditions. Four nonhalogenated VOCs (toluene, *m*- and *p*- xylenes, ethylbenzene, and benzene) had a negative correlation with dissolved oxygen indicating greater stability of these VOCs in anoxic conditions.

Recharge was the most important explanatory variable for 3 of the 14 VOCs, and was a significant explanatory variable

for an additional 6 VOCs (Table 5). Increased recharge was associated with increased detections of VOCs, with the exception of bromodichloromethane.

Land-use activity (year of construction, population density, MTBE use) was the most important explanatory variable for 3 of the 14 VOCs, and there was at least one significant land-use activity for all 14 VOCs. All variables listed in Table 5, except dissolved oxygen, recharge, and well depth, were associated with land-use activities. Year of construction (median year of home construction) was a significant variable for 7 of the 14 VOCs. As the age of the homes increased, the detection of some VOCs increased. Perhaps the increased age allowed more time for contamination to reach groundwater. Leaking sewer lines and septic systems can introduce VOCs into shallow groundwater; furthermore, leaking sewer lines and effluent from septic systems also would provide additional recharge to carry VOCs to shallow groundwater. Increased densities of sewer and septic systems were associated with increased detections of bromodichloromethane, chloroform, chloromethane, toluene, and ethylbenzene. Population density had a positive correlation with three halogenated VOCs (TCA, bromodichloromethane, and TCE), but negative correlation with two nonhalogenated VOCs (toluene and TMB, Table 5).

Discussion

The detection of VOCs in shallow groundwater in urban areas is controlled by factors related to source, transport, and fate of VOCs. The sources of VOCs have to be of sufficient strength to endure attenuation in the unsaturated zone and along the groundwater flow path to the sampled monitoring well. VOC detections were associated with certain types of land-use activity (for example, septic systems and sewer lines). The location, timing, extent, and nature of point source contamination is not always well documented; however, based on the information available, logistic regression analysis showed that point-source contamination was not strongly associated with detection of VOCs. The only VOC that showed an association with potential point source contamination in the final model was TMB (Table 5); however, the density of gasoline storage tanks for TMB was the weakest among five explanatory variables. There were only seven monitoring wells that even had a dry cleaner within 500 m of the well and yet PCE was detected in 144 samples. Either the source of PCE lies beyond 500 m, or dry cleaners are not the source of the PCE detected in urban land-use studies.

The transport of VOCs can occur with movement of natural groundwater recharge through the unsaturated zone, but

TABLE 5. Logistic Regression Analysis for 14 Most Frequently Detected VOCs

compound	independent variable	unstandardized coefficient	standardized coefficient	Hosmer/Lemeshow statistic
chloroform	dissolved oxygen	0.38	0.45	<0.01
	industry	-0.07	-0.13	
	vacant land	-0.03	-0.12	
	parks	-0.02	-0.10	
	ln(sewer density)	0.09	0.09	
bromo-dichloromethane	dissolved oxygen	0.33	0.28	0.20
	ln(sewer density)	0.29	0.19	
	parks	-0.05	-0.16	
	recharge (cm/year)	-0.04	-0.14	
	year of construction	-0.03	-0.10	
PCE	year of construction	-0.04	-0.21	0.89
	dissolved oxygen	0.16	0.18	
	water	-0.08	-0.14	
	parks	-0.03	-0.13	
TCE	ln(population density)	0.45	0.16	0.45
	year of construction	-0.03	-0.10	
TCA	dissolved oxygen	0.22	0.26	0.06
	ln(population density)	0.26	0.15	
	recharge (cm/year)	0.03	0.13	
1,1-DCA	dissolved oxygen	-0.28	-0.22	0.63
	recharge (cm/year)	0.05	0.14	
	year of construction	-0.03	-0.09	
	industry	0.04	0.06	
chloromethane	well depth (meters)	-0.06	-0.22	0.14
	ln(sewer density)	0.19	0.09	
	recharge (cm/year)	0.04	0.08	
	year of construction	-0.02	-0.05	
toluene	dissolved oxygen	-0.15	-0.20	0.15
	year of construction	-0.03	-0.19	
	ln(septic system density)	0.16	0.18	
benzene	dissolved oxygen	-0.12	-0.13	0.14
	industry	0.06	0.11	
ethylbenzene	recharge (cm/year)	0.04	0.16	0.70
	single family housing	0.02	0.14	
	ln(septic system density)	0.15	0.13	
	dissolved oxygen	-0.13	-0.13	
TMB	ln(population density)	-0.49	-0.28	0.70
	ln(septic system density)	-0.24	-0.25	
	recharge (cm/year)	0.05	0.21	
	water	0.07	0.16	
	gasoline storage tank density	0.92	0.15	
o-xylene	recharge (cm/year)	0.04	0.13	0.45
	ln(sewer density)	-0.20	-0.12	
m- and p-xylenes	recharge (cm/year)	0.04	0.19	0.18
	single family housing	0.02	0.16	
	dissolved oxygen	-0.12	-0.14	
	ln(sewer density)	-0.13	-0.11	
MTBE	MTBE use	2.23	0.36	0.96
	year of construction	-0.05	-0.25	
	recharge (cm/year)	0.04	0.20	

also can be augmented by anthropogenic activity such as irrigation and installation of dry wells. Increased recharge provides that transport mechanism to shallow groundwater, but also can decrease residence time for degradation/transformation to occur within the unsaturated zone. Thus, all other factors being equal, the occurrence of VOCs in urban areas would be expected to be higher in groundwater in the Eastern United States because of higher recharge rates in that area. However, studies in the Eastern United States did not have the largest detection frequencies of VOCs, because of differences in factors such as dissolved oxygen concentrations and land use.

Recharge was more strongly correlated with nonhalogenated VOCs compared with halogenated VOCs. This as-

sociation may indicate that nonhalogenated compounds require quick transport with recharge water before degradation occurs within the unsaturated zone; in contrast, halogenated VOCs can be transported to the water table even if recharge is low.

The fate of VOCs in shallow groundwater was strongly controlled by dissolved oxygen concentrations. The logistic regression model results showed that four halogenated VOCs (chloroform, PCE, TCA, and bromodichloromethane) were associated with larger oxygen concentrations; however, 1,1-DCA was associated with smaller concentrations of oxygen. There were four nonhalogenated VOCs (toluene, *m*- and *p*-xylenes, ethylbenzene, and benzene) associated with smaller oxygen concentrations. These associations generally are

supported by biodegradation studies (28) assuming increased detection frequency is due to greater compound stability.

Biodegradation is evident in this analysis because of the importance of dissolved oxygen concentrations in explaining the presence, absence, and concentrations of particular VOCs; however, some bacteria may be unable to maintain or attain a high metabolic activity on compounds present at ng/L or low $\mu\text{g/L}$ concentrations, which may prevent rapid degradation in the natural environment (29). A decline in degradation rate with concentration may explain why some VOCs are even detected in water with a median age of 10 years. For example, the 75th percentile VOC concentrations for the urban land-use studies ranged from ng/L to low $\mu\text{g/L}$ —much lower than mg/L concentrations used in almost all studies reporting rate constants (28). The residence time required for the 75th percentile concentrations to degrade to 0.001 $\mu\text{g/L}$ (lowest measured concentration for any VOC) can be calculated to determine whether published rate constants (28) seem reasonable for the low concentrations detected in this study. A residence time of multiple years seems reasonable for frequently detected VOCs assuming the water is about 10 years old. Under oxic conditions, the 75th percentile concentrations of PCE would degrade to 0.001 $\mu\text{g/L}$ in two years (mean published rate constant may be reasonable); in contrast, 1,1-DCA, TCA, TCE, benzene, toluene, and xylenes would be undetected within a few months (these VOCs probably have lower rate constants at these concentrations than indicated in the literature). Under anoxic conditions, the 75th percentile concentrations of 1,1-DCA, benzene, and TCE should degrade to 0.001 $\mu\text{g/L}$ in 4 or more years. TCA, PCE, xylenes, and toluene should degrade in 1 year or less.

Implications. It is not known in our studies whether VOCs detected in shallow groundwater in urban areas were transported to deeper groundwater; travel times may be sufficiently large so that degradation/transformation or dilution occurs before VOCs reach the deeper aquifers. The NAWQA program is currently addressing the issue of transport of anthropogenic and natural contaminants to public supply wells. The transport of contaminants to supply wells has additional groundwater flow complexities that were not addressed in urban land-use studies. For example, Stackelberg et al. (30) showed in one study that the number and total concentration of VOCs in water from deeper public supply wells were larger than those found in water from shallow monitoring wells. Groundwater withdrawal from these public supply wells may have resulted in increased risk of contamination compared to randomly located shallow urban monitoring wells (30). Longer flow paths and larger contributing areas for public supply wells were thought to integrate point source contamination sites making public supply wells more susceptible to VOC point-source contamination compared to shallow monitoring wells.

Nonpoint-source contamination seems to be a likely source of low concentrations of VOCs in shallow groundwater within new residential/commercial areas; however, there is a lot of unexplained variance in the data. More work needs to be done on potential nonpoint-source contamination from sewer and septic systems, retention and detention basins, dry wells for stormwater runoff, drainage ditches, transportation arteries, and stormwater sewers. More detailed analyses of locations, VOCs released, and groundwater flow analysis for point-source contamination sites in new residential/commercial areas are needed to verify that such contamination does not explain VOCs detected. Perhaps the extent of contamination from point source contamination is larger than that which was assumed in this analysis.

Point source contamination may be more important in other parts of urban development (for example, old residential/commercial, industrial areas, and major transportation corridors) not examined by NAWQA's urban land-use

studies of new residential/commercial development. Within the 17 large metropolitan areas investigated, LUST density is 3.5 times larger in areas not investigated by NAWQA's urban land-use studies. The larger LUST density may indicate increased risk from point source contamination in these other areas.

Recent urban development has affected shallow groundwater quality, but VOC concentrations are low. The frequent detections of VOCs are an indication that these aquifers are susceptible to anthropogenic contamination. There may be other anthropogenic contaminants, for example pesticides, pathogens, and pharmaceuticals, which may be transported to shallow groundwater and warrant investigation. The health risk associated with these mixtures of anthropogenic contaminants needs to be investigated.

To define the fate of VOCs associated with nonpoint source contamination, more degradation studies need to be conducted at low micrograms-per-liter concentrations, similar to Baehr et al. (31). Currently published rate constants for some VOCs may not be meaningful for these low concentrations. Transformation products also need to be defined in environmental samples. In some situations, transformation products may increase the number of VOCs present. The health effects of the most frequently detected mixtures, or those that are likely to be toxic, could be investigated.

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Supporting Information Available

Tables A1–A3 of statistical summary of VOCs in groundwater samples, concentration data, and common synonyms and abbreviations of selected VOCs, respectively. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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