

Atmosphere-Water Interaction of Chloroform, Toluene, and MTBE in Small Perennial Urban Streams

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ABSTRACT

An initial goal of the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program is to determine the frequency of occurrence and concentrations of a wide range of anthropogenic and natural compounds in the Nation's surface and ground water. A large number of contaminants are being monitored including volatile organic compounds (VOCs), pesticides, nutrients, and trace elements. As the NAWQA Program enters its second decade of studies, increased emphasis is being placed on identifying the source(s) and pathway(s) of frequently detected compounds. Chloroform, toluene, and methyl *tert*-butyl ether (MTBE) are frequently detected VOCs in the atmosphere, surface water, and ground water in urban watersheds and are the focus of this preliminary evaluation of the interaction of these compounds between the atmosphere and perennial urban streams. Air VOC samples were collected from four sites, and stream-water VOC samples were collected from two sites. The air concentrations were used to calculate water-equilibrium concentrations. These water-equilibrium concentrations then were compared to the measured stream-water concentrations to infer the predominant source of the VOCs. Results suggest that the atmosphere may not be the predominant source of chloroform and toluene in the two urban streams. In contrast, MTBE may be coming from the atmosphere, but further study would help to confirm that contributions from other sources are not important.

INTRODUCTION

An initial goal of water-quality sampling in the U.S. Geological Survey's (USGS) National Water-Quality Assessment (NAWQA) Program during the first cycle of studies (1991-2001) is to determine the frequency of occurrence and concentrations of a wide range of anthropogenic and natural compounds in the Nation's surface and ground water.

To accomplish this broad objective, a wide range of contaminants are being monitored including volatile organic compounds (VOCs), pesticides, nutrients, and trace elements.

Those compounds found to occur frequently in surface water or ground water warrant further investigation to determine the source(s) of such contamination and the pathway(s) by which compounds are entering water resources. As the NAWQA Program enters its second decade, increased emphasis is being placed on identifying the source(s) and pathway(s) of frequently detected compounds, as well as further understanding the trends and environmental effects of frequently detected compounds.

Fifty-five VOCs have been selected for emphasis in the NAWQA Program on the basis of: human health and aquatic toxicity information; Federal regulations and advisories; past detection in surface water, ground water, and drinking water; and potential for large-scale use in commerce.¹ In addition, 33 other VOCs are included on the VOC analytical schedule because of their potential emerging significance in drinking water. Preliminary national NAWQA Program findings for VOCs in untreated, ambient ground water have been reported.^{2,3} The NAWQA Program is also monitoring small, perennial urban streams for a wide range of VOCs as part of studies in large metropolitan areas to ascertain the water-quality consequences of urbanization. The primary focus of the urban studies is nonpoint-source contamination from new commercial-residential developments. Because of this focus, perennial streams selected for sampling do not contain large point-source effluents, although small effluent discharges may be present in some watersheds. Details of the sampling design of these urban stream sites, which in NAWQA are referred to as “urban intensive fixed sites,” are provided elsewhere.⁴

Sampling for VOCs has been completed or is in progress at 19 urban intensive fixed sites throughout the Nation. Frequent detection of low-level concentrations of some VOCs in urban streams is evident from preliminary analysis. Frequently detected VOCs in urban streams include toluene (55% of samples), chloroform (51%), methyl *tert*-butyl ether (MTBE) (40%), acetone (37%), trichloroethene (34%), tetrachloroethene (34%), *cis*-1,2-dichloroethane (31%), carbon disulfide (30%), and *m*&*p*-xylene (27%). These preliminary results have stimulated follow-up studies to define the most likely source(s) of the frequently detected compounds. These follow-up studies are focusing on the movement of VOCs between the urban atmosphere and urban streams. Ascertaining whether VOCs are volatilizing from these streams, or if the streams are in equilibrium with urban air, and if all of the frequently detected VOCs are reacting similarly, is of interest in determining the predominant source(s).

Many VOCs are detected frequently at low levels in urban air⁵, and the potential significance of the atmosphere in explaining detections of some VOCs in urban stormwater and shallow urban ground water has been discussed elsewhere.^{6,7,8} The focus of this paper is atmosphere–urban stream interaction for perennial streamflow (most NAWQA VOC samples are collected during base flow) in small urban watersheds that are dominated by new commercial–residential development. Previous studies have focused on stormwater whereas this study’s focus is on perennial streamflow.

Previous papers indicate that VOCs in the atmosphere eventually can reach equilibrium with VOCs in surface water, and in particular, it is known that precipitation quickly equilibrates with VOCs in the air.^{9,10} The water-equilibrium concentration of a VOC (C_e , mol/m³) is a function of the concentration in the air (C_a , mol/m³) and the dimensionless Henry’s law constant, H' , which is the air/water concentration ratio.

Equation 1. Calculation of the water-equilibrium concentration.

$$C_e = \frac{C_a}{H}$$

When concurrent measurements of VOCs in air and streams are made, these measurements can be used to ascertain if VOCs are expected to enter a stream from the atmosphere, if stream VOCs are expected to volatilize to the atmosphere, or if a state of equilibrium exists.

The purpose of this paper is to present preliminary findings from concurrent air-water monitoring at two of NAWQA's urban intensive fixed sites sampled in 1996-98. These results provide insights on the direction of VOC fluxes at the two locations. Chloroform, toluene, and MTBE were selected for this analysis because all three of these compounds frequently occur in both urban air and in urban streams at these sites.

STUDY METHODS

Ambient Air Sampling and Analytical Methods

The air sampling and analytical method are described briefly in the following paragraphs. For a more detailed discussion, see Pankow et al.¹¹ Two sorbent cartridges were used to collect the air samples. The first was a low-volume cartridge (with a sampling volume of approximately 1.5 liters) that is used to trap chlorofluorocarbons and other compounds with low breakthrough volumes. This cartridge contained 50 milligrams (mg) of Carbotrap B in series with 280 mg of Carboxen 1000 (Supelco Inc., Bellefonte, PA). The second was a high-volume cartridge (with a sampling volume of approximately 5 liters) that was used to trap the remaining 79 VOC analytes included in the analytical method. This cartridge contained 180 mg of Carbotrap B in series with 70 mg of Carboxen 1000 (Supelco Inc., Bellefonte, PA). Air samples were drawn through the cartridges using a programmable sampling pump (224-PCXR8, SKC Inc., Eight Four, PA). In addition, California Air Resources Board (CAARB) samples were collected using 6-liter Summa canisters as part of the California ambient air monitoring network.¹² All of the samples were 24-hour composite samples.

VOCs were analyzed by adsorption/thermal desorption gas chromatography/mass spectrometry (GC/MS). Detections less than the lowest daily standard were reported as estimated (E) values. The 87 VOCs analyzed ranged in volatility from CFC-12 to 1,2,3-trichlorobenzene. The analytes consisted of 27 halogenated alkanes, 12 halogenated alkenes, 5 ethers, 2 alcohols, 2 nitriles, 4 esters, 3 ketones, 30 aromatics, 1 disulfide, and 1 furan. Method detection limits for the analytes ranged from 0.02 to 0.06 parts per billion by volume (ppb_v). The CAARB air VOC samples also were analyzed by GC/MS.¹²

Each measured air VOC concentration was converted to a water-equilibrium concentration on the basis of the Henry's law constant (see equation 1) for that compound. Because the Henry's law constant for each compound is temperature dependent, the Arrhenius' relationship^{13,14} (equation 2) was used to calculate the Henry's law constant for specific temperatures for chloroform, toluene, and MTBE:

Equation 2. Arrhenius relationship for calculating a temperature dependent Henry's law constant.

$$H = \exp\left(A - \frac{B}{T}\right),$$

where H has dimensions of Pa-m³/mole, A and B are compound specific regression coefficients, and T is the temperature in Kelvin (°K). The compound specific coefficients for chloroform, toluene and MTBE for the Arrhenius relationship are given in Table 1.

Table 1. Arrhenius' relationship coefficients for chloroform, toluene, and MTBE.

Compound	A	B	Temperature range (°K)	R^*	Reference
Chloroform	20.63	4,382	275.15-298.15	0.997	13
Toluene	20.81	4,317	275.15-298.15	0.996	13
MTBE	30.06	7,721	298.15-323.15	0.981	14

* R , correlation coefficient.

Surface-Water Sampling and Analytical Methods

To assure consistent and representative VOC surface-water sample collection as part of the NAWQA Program, a sampler and guidelines for the collection of VOC samples from streams was developed. The sampler and sampling guidelines are described elsewhere.¹⁵ This sampler was used to collect stream-water samples for subsequent low-level analysis of VOCs.¹⁵ The sampler is designed to collect a grab sample at the mid-depth and centroid of the stream. The sampler simultaneously collects four 40-mL vials from inlet ports. The vials fill and overflow about 7 times, displacing the air in the vials and sampler body through an exhaust tube. In very shallow streams where the VOC sampler could not be submerged, representative samples were obtained manually by immersing an open 40-mL vial near the centroid of streamflow.

All stream sampling sites were near streamflow-gaging stations because stream discharges associated with contaminant concentrations were needed to evaluate relations between streamflow and water-quality characteristics.^{4,16} Samples were collected from relatively straight channel reaches where uniform flow existed. Sampling sites directly downstream from direct sources of contamination were avoided to achieve environmentally representative samples. Stream-water samples were preserved with 1:1 hydrochloric acid to a pH of 2 and kept chilled until analyzed.

The analytical method for the water samples is described in detail elsewhere.¹⁷ Briefly, the method consisted of purge-and-trap GC/MS using a 25-mL sample. Compounds were identified by strict qualification criteria, which included analyzing standard reference materials and comparing retention times and relative ratios of the mass spectra. Compounds were quantitated from internal standard procedures. Quantitation below the lowest calibration standard was qualified as estimated (E) to signify less confidence in the extrapolated concentration.¹⁷ The analytical method quantified 85 VOCs at sub-microgram-per-liter (µg/L) concentrations.

SAMPLING SITES AND SAMPLES COLLECTED

Ambient air samples were collected by USGS personnel from three sites in the southern New Jersey area¹⁸ and at one site in Roseville, CA. In addition, CAARB collected samples at the Roseville, CA, site were also used in the analysis to increase the period of record at the site. The three sites in southern New Jersey and the one site at Roseville, CA, represented a range of traffic and population densities. The southern New Jersey sites are located within the Philadelphia, PA-Wilmington, DE-Atlantic City, NJ, consolidated metropolitan statistical area (CMSA), and the Roseville, CA, site is located in the Sacramento-Yolo, CA, metropolitan statistical area (MSA). The three sites in southern New Jersey had vehicular traffic that ranged between relatively low traffic (rural road) to relatively high traffic (four-lane expressway).⁷ The Roseville, CA, site was a suburban site with high traffic (arterial highway).¹²

Ambient air data were collected between 4/29/1997 and 10/07/1999 from the southern New Jersey sites and between 8/02/1997 and 9/14/1998 from the Roseville, CA, site. CAARB ambient air VOC data were obtained from the Roseville, CA, site to increase the period of record for this site prior to 8/02/1997. Only the air VOC data that closely corresponded, within 10 days, to surface-water sampling dates were included in this study (4/29/1997 to 3/17/1998 for the southern New Jersey sites--28 samples, and 10/30/1996 to 4/23/1998 for the Roseville, CA, site--30 samples). Twenty of the 30 Roseville, CA, samples were collected and analyzed by CAARB. Temperature ranges over the sampling period were 272-301°K and 279-299°K for southern New Jersey and Roseville, CA, respectively.

Stream samples were collected from two urban intensive fixed sites -- Great Egg Harbor River near Sicklerville, NJ, and Arcade Creek near Del Paso Heights, CA. The Great Egg Harbor River site was located in the Philadelphia, PA-Wilmington, DE-Atlantic City, NJ, CMSA, and the Arcade Creek site was located in the Sacramento-Yolo, CA, MSA. The surface-water sites were within a 25-km radius of the air sampling sites. Surface-water VOC samples were collected between 4/01/1996 and 07/14/1998 from the Great Egg Harbor River and between 11/06/1995 and 4/23/1998 from Arcade Creek. Only those stream data that had closely corresponding air-sample data were included in the analysis for this paper (between 4/30/1997 and 3/17/1998 for Great Egg Harbor River and between 10/29/1996 and 4/23/1998 for Arcade Creek). A brief description of the drainage basin for each site is given in Table 2.

RESULTS

The ambient air samples for specific dates from the three southern New Jersey sites were averaged prior to comparison to the measured stream data. The Roseville, CA, data were only averaged when more than one sample from each laboratory were collected on the same date. The average air concentrations then were converted to calculated water-equilibrium concentrations using the Henry's law constant corrected for the average daily air temperature.

Table 2. Surface-water sampling-site descriptions.

Characteristic	Sampling site	
	Great Egg Harbor River near Sicklerville, NJ	Arcade Creek near Del Paso Heights, CA
USGS Station ID	01410784	11447360
Drainage Area (square kilometers)	39.1	86.8
Population Density (people/square kilometer)	369	1,881
Mean Annual Flow (cubic meters/second)	0.58	0.48
Annual Precipitation (centimeters)	111	47.3

An overall statistical summary of the ambient air, calculated water-equilibrium, and stream-water data is given in Table 3. The measured ambient air concentrations ranged from not detected (ND) to E0.07 ppb_v, ND to 2.0 ppb_v, and E0.16 to 2.1 ppb_v for chloroform, toluene, and MTBE, respectively. The measured stream-water concentrations ranged from ND to E0.10 µg/L, ND to 1.8 µg/L, and ND to 1.6 µg/L for chloroform, toluene, and MTBE, respectively.

Table 3. Summary statistics for ambient air, calculated water equilibrium, and stream-water concentrations.

Sample Medium	Number of Samples Analyzed	Number of Samples With a Detection	Statistic				Standard Deviation
			Minimum	Mean	Median	Maximum	
Chloroform							
Air, ppb _v	38	30	ND*	E0.02	E0.02	E0.07	0.017
Calculated water equilibrium, µg/L	30	30	0.0001	0.0014	0.0014	0.0035	0.0009
Measured stream water, µg/L	38	24	ND*	E0.02	E0.02	E0.10	0.02
Toluene							
Air, ppb _v	38	35	ND*	0.70	0.60	2.0	0.48
Calculated water equilibrium, µg/L	35	35	0.004	0.026	0.017	0.09	0.019
Measured stream water, µg/L	38	28	ND*	0.16	0.09	1.8	0.30
MTBE							
Air, ppb _v	38	38	E0.16	0.82	0.85	2.1	0.43
Calculated water equilibrium, µg/L	38	38	0.03	0.35	0.25	1.7	0.30
Measured stream water, µg/L	38	32	ND*	0.40	0.30	1.6	0.40

*ND, not detected.

Figure 1. Calculated water-equilibrium concentrations versus measured stream-water concentrations for chloroform, toluene, and MTBE.

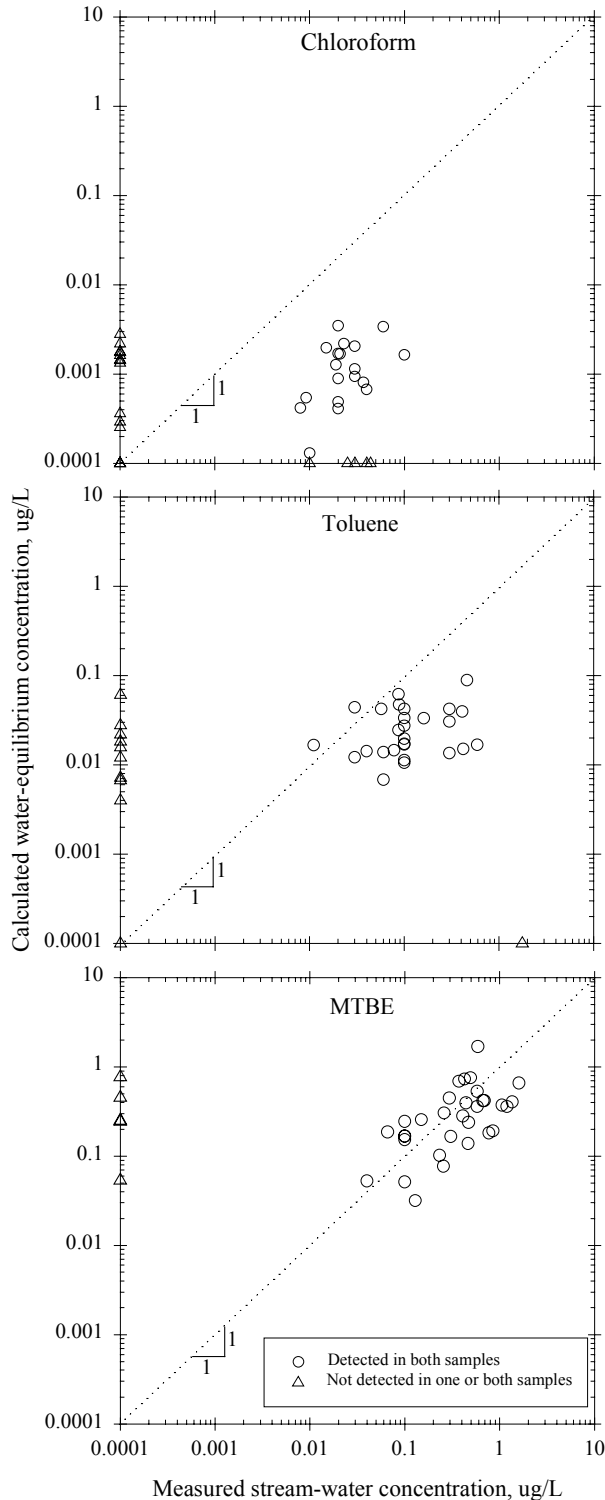


Figure 1 shows the calculated water-equilibrium concentrations versus the measured stream-water concentrations. The measured stream-water concentrations for chloroform were much higher than the calculated water-equilibrium concentrations. In contrast, the stream-water concentrations of MTBE plot near and both above and below the 1-to-1 line. Toluene’s measured stream-water concentrations were intermediate between chloroform and MTBE.

The general magnitudes of the differences between the calculated water-equilibrium concentrations and the measured stream-water concentration are evident also in the mean and median statistics given in Table 3. The mean and median calculated water-equilibrium concentrations of chloroform from air samples are approximately one order of magnitude less than the measured stream-water concentrations. Mean and median MTBE concentrations for the two data sets were very similar, although the measured stream-water concentrations were slightly larger than the calculated water-equilibrium concentrations from ambient air VOC samples. Toluene’s mean and median concentrations were intermediate between chloroform and MTBE.

The Wilcoxon signed-rank test was used to determine whether there were statistically different differences between the measured stream concentrations and the calculated water-equilibrium concentrations. The signed-rank test usually is stated as a determination of whether the paired data come from the same population.¹⁹ If the measured stream concentrations and the calculated water-equilibrium concentrations are from the same

population, about one-half of the differences will be less than 0 and one-half will be greater than 0. The Wilcoxon signed-rank test showed a significant difference for chloroform and toluene data ($p=0.0000$) indicating that the two data sets were different. In contrast, the difference of the paired MTBE data were not significantly different ($p=0.0509$) suggesting that the two data sets were similar. These statistical results agree favorably with data presented in Table 3 and Figure 1.

DISCUSSION

These preliminary results can be compared with previous studies by Delzer et al.²⁰ and Lopes and Bender⁶ for VOCs in stormwater. Delzer et al.²⁰ reported median concentrations of detections of 0.7, 0.3, and 1.5 $\mu\text{g/L}$ for chloroform, toluene, and MTBE, respectively. The median stream-water concentrations detected in this study were 0.02, 0.09, and 0.30 $\mu\text{g/L}$ for chloroform, toluene, and MTBE, respectively. The frequencies of detection in stormwater from Delzer et al.²⁰ and Lopes and Bender⁶ were 13%, 23%, and 7% for chloroform, toluene, and MTBE, respectively. The frequencies of detection for stream-water samples in this study were 63%, 74%, and 84% for chloroform, toluene, and MTBE, respectively. The differences in the median concentrations and the frequencies of detection may be attributed, in part, to the low-concentration analytical method used in this study and the differences in the source of water sampled, namely, stormwater in Delzer et al.²⁰ and Lopes and Bender⁶ versus perennial streamflow in this study.

On the basis of Figure 1 and the statistical results in Table 3, chloroform and toluene were not in a state of equilibrium between the air and the stream water. Furthermore, stream water concentrations were larger than expected levels from the air VOC measurements. These conditions suggest that the atmosphere may not be the predominant source of chloroform or toluene to the stream. These two VOCs may have a predominant point source(s) or land-based nonpoint source(s) within the watersheds. The results for MTBE were different from chloroform and toluene. MTBE was relatively close to being in equilibrium between the air and the stream water. This result would be consistent with urban air and(or) precipitation being the predominant source of MTBE to the streams. However, further study to identify other MTBE sources would help to verify this preliminary interpretation.

There is a wide variety of possible sources for chloroform in surface waters.²¹ It is widely known that chloroform is a major disinfection by-product of the chlorination treatment process. Possible sources of chloroform to surface water include ground-water base flow, incidental overland flow from the irrigation of lawns and parks, treatment-plant effluents, and other sources of chlorinated water.²¹

Possible sources of toluene include effluents from industrial wastewater²¹, sewage effluent²¹, and stormwater runoff from gasoline-tainted roadways and parking areas.⁶ Other possible sources of toluene is ground water containing toluene from gasoline and solvent releases, and the effluent from gasoline-station remediation/treatment systems.

Lopes and Bender⁶ stated that, "urban air could be an important nonpoint source of MTBE in stormwater..." MTBE sources also could be associated with runoff from parking lots or streets, and industrial wastewater effluents similar to other gasoline-

related hydrocarbons.²¹ Another source may be ground-water inflows upstream from the sampling sites, containing MTBE that has begun to volatilize out of the water column.

CONCLUSIONS

The results of this preliminary study suggest that the atmosphere is not the dominant source of the chloroform or toluene measured in the streams sampled. The calculated water-equilibrium concentrations for chloroform were about 10% of the concentration detected in the measured stream-water samples. This suggests that the presence of chloroform and toluene in the two streams in this study are dominated by either ground-water inflow, overland flow, or small effluents containing concentrations larger than what may be explained by equilibrium with the atmosphere.

The results show that the measured stream-water concentrations for MTBE are close to equilibrium with the atmosphere. This suggests that MTBE may be coming from the atmosphere in low concentrations, but further study would help to confirm that contributions from other sources are not important.

CONTINUING WORK

This study has been expanded to include six additional urban intensive fixed sites in other areas of the country with co-located concurrent air VOC and stream VOC sampling. Sampling at these sites was initiated in spring 1999 and is scheduled to be completed in mid-2000. Follow-up water sampling is planned also for a subset of the six sites to help further determine the source(s) of VOCs to urban streams. As part of the effort, samples will be collected from the stream and bed sediment, ground-water inflows to the streams, from small effluents, if any, and from other inflow to the streams, along with concurrent ambient air VOC samples. In addition to other monitoring sites and synoptic sampling, future interpretive analysis is planned to include other VOCs frequently detected in both urban air and urban streams.

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KEYWORDS

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