

APPLICATION OF A SOURCE APPORTIONMENT MODEL IN CONSIDERATION OF VOLATILE ORGANIC COMPOUNDS IN AN URBAN STREAM

WILLIAM E. ASHER,^{†‡} WENTAI LUO,[‡] KIMBERLY W. CAMPO,[§] DAVID A. BENDER,^{||} KEITH W. ROBINSON,[#]

JOHN S. ZOGORSKI,^{||} and JAMES F. PANKOW*[‡]

[†]Air–Sea Interaction and Remote Sensing Department, Applied Physics Laboratory, University of Washington, Seattle, Washington 98105, USA

[‡]Department of Environmental and Biomolecular Systems, Oregon Graduate Institute School of Science and Engineering, Oregon Health and Science University, Beaverton, Oregon 97006-8921, USA

[§]U.S. Geological Survey, 10 Bearfoot Road, Northborough, Massachusetts 01532

^{||}U.S. Geological Survey, 1608 Mountain View Road, Rapid City, South Dakota 57702

[#]U.S. Geological Survey, 361 Commerce Way, Pembroke, New Hampshire 03275-3719

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Abstract—Position-dependent concentrations of trichloroethylene and methyl-*tert*-butyl ether are considered for a 2.81-km section of the Aberjona River in Massachusetts, USA. This river flows through Woburn and Winchester (Massachusetts, USA), an area that is highly urbanized, has a long history of industrial activities dating to the early 1800s, and has gained national attention because of contamination from chlorinated solvent compounds in Woburn wells G and H. The river study section is in Winchester and begins approximately five stream kilometers downstream from the Woburn wells superfund site. Approximately 300 toxic release sites are documented in the watershed upstream from the terminus of the study section. The inflow to the river study section is considered one source of contamination. Other sources are the atmosphere, a tributary flow, and groundwater flows entering the river; the latter are categorized according to stream zone (1, 2, 3, etc.). Loss processes considered include outflows to groundwater and water-to-atmosphere transfer of volatile compounds. For both trichloroethylene and methyl-*tert*-butyl ether, degradation is neglected over the timescale of interest. Source apportionment fractions with assigned values α_{inflow} , α_1 , α_2 , α_3 , etc. are tracked by a source apportionment model. The strengths of the groundwater and tributary sources serve as fitting parameters when minimizing a reduced least squares statistic between water concentrations measured during a synoptic study in July 2001 versus predictions from the model. The model fits provide strong evidence of substantial unknown groundwater sources of trichloroethylene and methyl-*tert*-butyl ether amounting to tens of grams per day of trichloroethylene and methyl-*tert*-butyl ether in the river along the study section. Modeling in a source apportionment manner can be useful to water quality managers allocating limited resources for remediation and source control.

Keywords—Source apportionment Streams Volatile organic compounds Trichloroethylene Methyl-*tert*-butyl ether

INTRODUCTION

Multiple dissolved volatile organic compounds (VOCs) are frequently present in urban streams [1,2]. An adequate understanding does not exist of the identities and relative roles of the typical contaminant sources or of the coupled manners in which physical, chemical, and biological processes in streams act on those contributions to yield observed position- and time-dependent concentrations. Source apportionment (SA) modeling principles can be applied in determining how multiple VOC sources and sinks can combine to yield a given observed concentration at some stream point (x, y, z, t) . Reasons for interest in the relative and absolute contributions of different sources include the need to apportion the origins/responsibility for observed contamination as well as the associated risks to humans and ecosystems.

Pankow et al. [3] introduce the SA modeling framework used here. For each contaminant i and each stream point (x, y, z, t) (where x , y , and z are the along-flow, cross-flow, and vertical directions, respectively, and t is time), $\alpha_1, \alpha_2, \dots, \alpha_{N_s}$ are the SA fractions due to the N_s different sources acting along a stream,

$$\alpha_j = c_{w,j}/c_w \quad (1)$$

where c_w (mol/m³) is the total stream concentration of the contaminant of interest and $c_{w,j}$ (mol/m³) is the portion of c_w that is attributable to source j . For each contaminant of interest, $\alpha_1 + \alpha_2 + \dots + \alpha_{N_s} = 1$. Pankow et al. [3] discuss two SA rules that govern the calculation of α values for VOCs.

For equilibrium, Henry's gas law (HGL) partitioning of a given VOC is

$$c_g/c_w^S = H(T)/RT \quad (2)$$

where c_g (mol/m³) is the local air concentration of the compound, c_w^S (mol/m³) is the water concentration for saturation equilibrium with c_g , $H(T)$ (m³ Pa/mol) is the compound- and temperature-dependent HGL constant, R is the gas constant (8.314 m³ Pa K⁻¹ mol⁻¹), and T is temperature (K). On the stream surface, there are three possibilities [3]. First, $c_w > c_w^S$ (supersaturation), such that there is net volatilization of the compound from the stream surface to the air. Second, $c_w < c_w^S$ (undersaturation), such that there is net absorption of the compound from the air. Third, $c_w = c_w^S$ (equilibrium), such that there is zero net flux of the compound locally between the stream and air. Whenever $c_g > 0$, there will always be some invasive flux from the air to the water; whenever $c_w > 0$, there will always be some evasive flux from the water to the air.

* To whom correspondence may be addressed (pankow@ebs.ogi.edu).

The net flux is zero when the magnitudes of the invasive and evasive fluxes are equal (the equilibrium case).

Here, we provide an overview of StreamVOC, a one-dimensional numerical SA model for VOCs in streams. We also discuss model results obtained for a section of the Aberjona River located in Winchester (Massachusetts, USA); the model was initialized with data collected during a synoptic study conducted July 11–13, 2001.

MODEL DESCRIPTION

The StreamVOC model assumes that the flow past a fixed point is steady, all sources and sinks are steady, and vertical/lateral mixing at each x is complete and instantaneous. These assumptions simplify the functionality of each $c_w(x, y, z, t)$ to $c_w(x)$ and each $\alpha_j(x, y, z, t)$ to $\alpha_j(x)$. The model divides a stream into a finite number of separate, longitudinal zones. Zone boundaries are the particular distances x along the stream at which one or more of the following apply: Substantial change in h or w , confluence with a tributary, a point source that adds contaminant mass.

Each stream zone is considered to have a constant depth h (m) and a constant width w (m). Within a given zone, the stream flow Q (m^3/s) and velocity u (m/s) can change because of flow gains (or losses) from (to) groundwater. Within a given zone, contaminant mass can enter a stream from a distributed source (as from the nonpoint inflow of contaminated groundwater) or from the atmosphere. Contaminant mass can be lost by volatilization to the atmosphere, degradation, outflow of stream water to local groundwater, or a combination of these factors. Loss through degradation is modeled as a first-order rate process; partitioning to bed and suspended sediments is neglected.

The equations and parameterizations used in StreamVOC are described in *Supplemental Data* (online only; <http://dx.doi.org/10.1897/06-557.S1>). Briefly, StreamVOC integrates the set of coupled differential equations describing changes in c_w and α_j in a parcel of water by way of a Runge–Kutta routine [4]. (This numerical approach was used to maximize model flexibility in terms of the sources and groundwater outflows and to allow future adaptations to problems involving three-dimensional fluid motions.) The parcel is tracked in a Lagrangian fashion. Input data are required for temperature; w , h , and Q versus x ; locations and flow rates for the source inflows and loss outflows; VOC concentrations in the source flows and in the atmosphere; VOC diffusivities in water; and VOC H values for the temperature range of interest. Equation 2 is applied with H evaluated with the use of the waterside temperature. Air–water exchange is modeled by the two-film model [5], with resistances calculated as described by Rathbun [6]. For streams with $u \geq 0.04$ m/s and $h > 0.12$ m, the waterside resistance is based on relations involving u and h [7,8]. For streams with $u < 0.04$ m/s, the waterside resistance is based on wind speed alone [9]. Gas volatilization/absorption at dams and weirs is estimated according to Gulliver et al. [10].

StreamVOC offers a choice between the two methods of Pankow et al. [3] for calculating the effect of air–water exchange of VOCs on the SAs. In the net flux method, the VOC flux is expressed as the difference between the invasive flux and the evasive flux. In the individual fluxes method, the invasive and evasive fluxes are considered separately: Regardless of whether the system is at HGL equilibrium, whenever $c_g > 0$, the atmosphere is a source of atmospherically derived

VOC and the $\alpha_j(x)$ values are modified accordingly. A series of numerical experiments to investigate the performance of the model have been carried out by Asher et al. [11] with the use of methyl-*tert*-butyl ether (MTBE). The tests verified proper coding of mixing and dilution, air–water exchange, degradation, and volatilization at hydraulic structures.

STUDY SYSTEM AND MEASUREMENTS

Measurements and sampling in the Aberjona River

The study system is a 2.81-km section of the Aberjona River located in the watershed of the same name and found in Woburn and Winchester (Massachusetts, USA). The area is highly urbanized and has a long history of industrial activities dating back to the early 1800s [12]. Problematic contamination by chlorinated solvents has been found in Woburn wells G and H, which are public drinking water wells near the river. These two wells are located approximately five stream kilometers upstream from zone 1 of the study section. Possible health effects attributable to the wells have been chronicled by Harr [13]. Approximately 300 toxic release and hazardous sites are documented in the watershed upstream from the terminus of the study section. Figure 1 is an aerial image of the study region, which is in Winchester.

Surface water, groundwater, and atmospheric VOC concentrations were measured along the river study section for a synoptic study during July 11–13, 2001. Table 1 describes division of the study section into 10 zones on the basis of stream characteristics. Depth h , width w , and flow Q were measured on July 11, 2001. Table 1 includes average values for h and w in each zone, the measured values of Q , and the flow velocities u (as derived from h , w , and Q). For zone 7, which flows through a closed underground culvert for most of its length, the assumption was made that no air–water gas exchange occurred. Zone 8 contains two ponds connected by a short open channel. Each pond and the connecting channel was defined as a separate subzone. The water velocity u in each pond during the study period was < 0.04 m/s, and so air–water gas exchange in each was considered to be purely wind driven (in nearby Bedford, MA, USA, the average wind speed ≈ 2 m/s, as documented in historical records [14]; <http://ols.nndc.noaa.gov/plolstore/plsql/olstore.prodspecific?prodnum=C00353-CDR-S0001> and <http://www.wunderground.com/>). The confluence with Horn Pond Brook (HPB) was served as the boundary between zones 7 and 8a.

Two hydraulic structures in the study section were considered. One is a small dam located at the downstream end of zone 8c. The dam functions like a sharp-crested spillway in terms of its air–water exchange characteristics. The second structure is an ogee-crested weir located at the downstream end of zone 9. The dam and weir dimensions used in calculating gas exchange efficiencies were determined from digital photographs.

Surface water grab samples were collected at the upstream boundary of zone 1; at the downstream boundaries of zones 1 to 7, 8b, 8c, 9, and 10; and in HPB immediately upstream from its confluence with the Aberjona River. Sampling methods described elsewhere [15,16] were used. Groundwater samples were collected at the upstream boundary of zone 1 and the downstream boundary of zones 1, 3 to 7, and 8c to 10. Sampling occurred from approximately 1 m below streambed level with a drive point (15-cm screened interval), Teflon® tubing, and a peristaltic pump. Values of c_w for 87 VOCs were

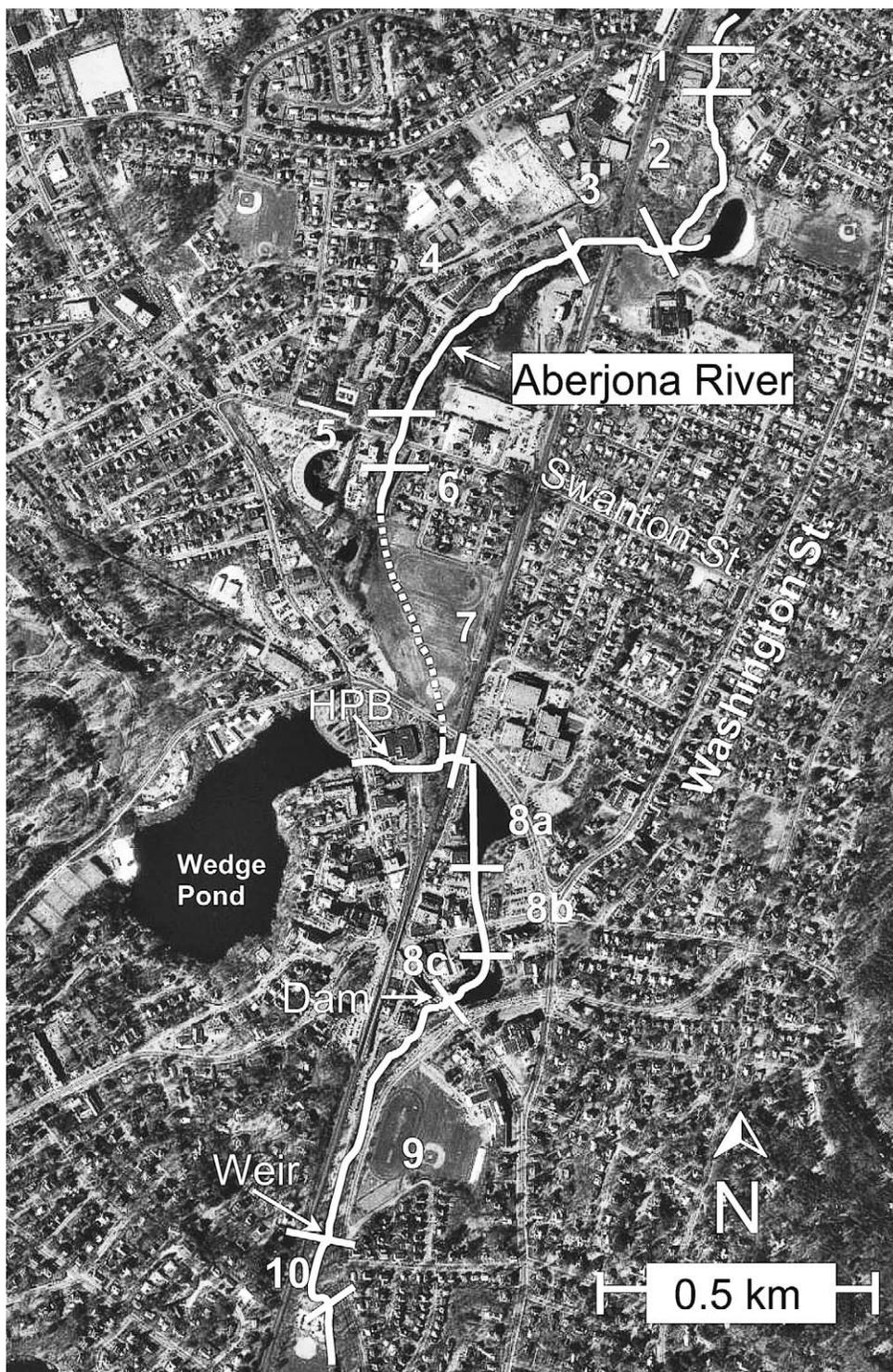


Fig. 1. An aerial view of the study section of the Aberjona River in Winchester (Massachusetts, USA), and the numbered stream zones. The river flows from the top of the image toward the bottom. The dashed line represents the buried culvert that composes most of zone 7. HPB = Horn Pond Brook (Massachusetts, USA). Woburn (Massachusetts, USA) is located upstream of the study section.

determined in all water samples by purge and trap followed by gas chromatography/mass spectrometry (GC/MS) according to the method of Connor et al. [17]. For each VOC with a nonzero c_w at the upstream boundary of zone 1, 100% of the initial VOC concentration was assigned to a source designated simply as the inflow: at the upstream boundary of the study section, $\alpha_{\text{inflow}} \equiv 1$. Each value of c_g was determined by a time-averaged (10-h) air sample obtained at a single point

(centroid of the synoptic study) at 1 m above the ground surface; the analytical method involved adsorbent cartridge sampling, followed by thermal desorption, then GC/MS (see Pan-kow et al. [18]). Acetone; benzene; MTBE; chloroform; 1,1-dichloroethane; *cis*-1,2-dichloroethene; trichloroethene (TCE); and perchloroethene (PCE) were detected in enough samples to allow meaningful comparisons of measured and model-predicted concentrations. Results for TCE and MTBE are con-

Table 1. Synoptic hydrological data for a study section of the Aberjona River (Massachusetts, USA) collected July 11–13, 2001

| Zone | Upstream boundary (km) | Downstream boundary (km) | Average width, w (m) | Average depth, h (m) | Flow at up-stream boundary, Q (m ³ /s) | Change in flow over the zone, ΔQ (m ³ /s) | Average flow velocity, u (m/s) |
|------------------|------------------------|--------------------------|------------------------|------------------------|---|--|----------------------------------|
| 1 | 0 | 0.096 | 5.5 | 0.30 | 0.3540 | +0.0368 | 0.226 |
| 2 | 0.096 | 0.400 | 7.3 | 0.53 | 0.3908 | +0.0227 | 0.104 |
| 3 | 0.400 | 0.540 | 7.9 | 0.76 | 0.4135 | +0.0925 | 0.0767 |
| 4 | 0.540 | 1.090 | 22.8 | 0.34 | 0.5060 | -0.173 | 0.0539 |
| 5 | 1.090 | 1.150 | 8.5 | 0.64 | 0.3330 | +0.0538 | 0.0664 |
| 6 | 1.150 | 1.230 | 7.3 | 0.79 | 0.3868 | -0.0595 | 0.0618 |
| 7 ^a | 1.230 | 1.647 | 3.6 | 0.37 | 0.3273 | -0.0264 | 0.233 |
| 8a | 1.647 | 1.897 | 100.0 | 2.0 ^b | 0.3009 | +0.0156 | 0.00256 |
| 8b | 1.897 | 2.147 | 10.0 | 2.0 ^b | 0.5185 | 0.0 | 0.0231 |
| 8c | 2.147 | 2.293 (dam spillway) | 90.0 | 2.0 ^b | 0.5185 | +0.0118 | 0.00292 |
| 9 | 2.293 | 2.736 (weir) | 10.7 | 1.07 | 0.5303 | +0.0311 | 0.0479 |
| 10 | 2.736 | 2.811 | 7.9 | 0.64 | 0.5614 | +0.0510 | 0.116 |
| HPB ^c | 1.647 | 1.647 | NA | NA | 0.202 | NA | NA |

^a This is a connecting culvert that is closed for most of its length.

^b Depths in ponds and connecting closed culvert estimated from historical records (not measured here).

^c HPB = Horn Pond Brook (Massachusetts, USA); NA = not available.

sidered here; results for the other compounds are discussed by Asher et al. [11].

Calculations

The total transit time for a parcel of water in the river study section was approximately 50 h. Available rate data indicate that degradation of TCE will not be substantial over this time-scale either abiotically or biotically ([19]; <http://www.atsdr.cdc.gov/>). Similar conclusions pertain to MTBE [6]. The method detection limit values for TCE and MTBE in water were 0.020 $\mu\text{g/L}$ and 0.025 $\mu\text{g/L}$, respectively. Surface water samples collected at the downstream end of zone 5 indicated the following relative difference between replicates: TCE 0.63%, MTBE 11%. Groundwater samples collected at the downstream end of zone 1 indicated the following relative difference between replicates: TCE 13%, MTBE 6.8%.

For calculation of air–water gas fluxes, H (m³ atm mol⁻¹) values are available as a function of temperature for both TCE [20] and MTBE [21]. Values of c_w^S were calculated with the measured c_g values. Values of the molar volume (m³/mol, for use in calculation of the waterside gas transfer velocity $k_{L,i}$ (m/s) as a function of local stream conditions according to Rathbun [6]) were obtained as liquid densities for both TCE [22] and MTBE [23].

The c_w values for both TCE and MTBE represented supersaturation ($c_w > c_w^S$) over the entire study section, and thus a net flux out of the river over the entire study section. For TCE, the measurements indicate c_w/c_w^S values on the order of approximately 10^3 , so that $\alpha_{\text{atm}}(x)$ was negligible both in the inflow and over the entire study section. For MTBE, c_w/c_w^S values were on the order of approximately 10, and the invasive component of the flux is calculated to have been approximately 7% of the evasive flux. Thus, according to the individual fluxes method to SA modeling of VOCs [3], a nonnegligible portion of the MTBE assigned to α_{inflow} at zone 1 might have originated in the atmosphere.

For each VOC, the StreamVOC model was initialized with the use of c_w as measured for the flow entering zone 1. Modeled VOC sources included inflows to the stream from groundwater and HPB. It was assumed for the sake of the modeling effort (but not known with certainty) that no point sources existed along the modeled length. Modeled VOC losses included volatilization and outflows from the stream to groundwater. Mod-

eling the inflow/outflow of VOCs from/to groundwater in each zone assumed that: inflow/outflow could be determined on the basis of the difference in Q values measured at the zone boundaries; inflow/outflow could be distributed uniformly over a given zone; and, when an inflow contained a VOC, the inflow concentration over the zone could be taken as being steady and equal to the value measured at the downstream end of the zone with drive-point sampling. The measured concentrations in the source inflows (Table 2) are denoted $c_{\text{source } l}^{\text{meas}}$. The index l can refer to any of the zones k in which groundwater inflow occurs, and to HPB. As an example of the implementation of the first assumption, Q at the upstream boundary of zone 3 was 0.4135 m³/s, and 0.5060 m³/s at the downstream end. With no other sources of flow acting in this zone, ΔQ , and thus the total inflow of groundwater over zone 3, was computed as 0.0925 m³/s (Table 1).

RESULTS

Both TCE and MTBE were undergoing net volatilization to the atmosphere over the entire study section. (The amount of that volatilization would not be sufficient to substantially affect local air quality.) Figures 2a and 3a provide plots of c_w versus distance for TCE and MTBE, respectively. The solid lines give modeled values (c_w^{mod}) obtained when taking the concentrations in the source inflows (groundwater flows and HPB), to be given by the $c_{\text{source } l}^{\text{meas}}$ values measured in the synoptic study, and assuming no other sources of any kind; the corresponding SA plots are given in Figures 2b and 3b.

For both TCE and MTBE, the reduced least squares estimator of the fit between the measured and model-predicted c_w is defined as

$$\phi_i^2 = \sum_{k=1}^{n_i} \frac{(c_{w,k}^{\text{meas}} - c_{w,k}^{\text{mod}})^2}{(c_{w,k}^{\text{meas}})^2} \quad (\text{degrees of freedom} = n_i) \quad (3)$$

where n_i is the number of surface water concentrations of i measured in the various zones during the synoptic study, $c_{w,k}^{\text{meas}}$ is the measured stream concentration of VOC i at the zone k sampling point, and $c_{w,k}^{\text{mod}}$ is the model-predicted concentration of i at the zone k sampling point. The values of ϕ_i^2 are similar for TCE and MTBE (Table 3).

It is extremely unlikely that any of the groundwater samples were collected at precisely the right point so as to have a concentration that exactly matched the true volume-averaged

Table 2. Measured and modeled stream concentrations of trichloroethylene (TCE) and methyl-*tert*-butyl ether (MTBE) for a study section of the Aberjona River (Massachusetts, USA), July 11–13, 2001 (assumed model temperatures: stream, 22°C; air, 20°C)^a

| Zone edge | <i>x</i> (km) | TCE <i>c_w</i> (μg/L) | | | MTBE <i>c_w</i> (μg/L) | | |
|------------------|---------------|---------------------------------|---|--|----------------------------------|---|--|
| | | Measured | Modeled with <i>c_{source l}^{meas}</i> | Modeled with <i>c_{source l}^{fit}</i> | Measured | Modeled with <i>c_{source l}^{meas}</i> | Modeled with <i>c_{source l}^{fit}</i> |
| 1—Upstream | 0 | 0.17 | NA | NA | 0.61 | NA | NA |
| 2—Upstream | 0.096 | 0.18 | 0.17 | 0.18 | 0.63 | 0.59 | 0.64 |
| 3—Upstream | 0.400 | 0.16 | 0.15 | 0.16 | 0.58 | 0.53 | 0.58 |
| 4—Upstream | 0.540 | 0.15 | 0.19 | 0.18 | 0.58 | 0.42 | 0.54 |
| 5—Upstream | 1.090 | 0.21 | 0.13 | 0.12 | 0.40 | 0.32 | 0.41 |
| 6—Upstream | 1.150 | 0.32 ^b | 0.26 | 0.33 | 0.51 ^b | 0.27 | 0.45 |
| 7—Upstream | 1.230 | 0.31 | 0.26 | 0.32 | 0.34 | 0.27 | 0.44 |
| 7—Downstream | 1.647 | 0.32 | 0.26 | 0.32 | 0.54 | 0.27 | 0.44 |
| 8c—Upstream | 2.147 | 0.18 | 0.14 | 0.20 | 0.99 | 1.53 | 1.08 |
| 9—Upstream | 2.293 | 0.18 | 0.083 | 0.19 | 0.80 | 1.05 | 0.74 |
| 10—Upstream | 2.736 | 0.16 | 0.075 | 0.20 | 1.43 | 1.03 | 1.68 |
| 10—Downstream | 2.811 | 0.16 | 0.056 | 0.17 | 1.36 | 0.82 | 1.34 |
| HPB ^c | 1.647 | 0.035 | NA | NA | 4.12 | NA | NA |

^a NA = not applicable.

^b Average for two grab samples.

^c HPB = Horn Pond Brook (Massachusetts, USA).

concentration for the corresponding inflow. Moreover, in any such study, there is always some chance that one or more sources will be missed, leading to subsequent underpredictions in modeled concentrations. The model was therefore rerun in an optimization mode, wherein the concentration values for the source inflows (including HPB, but not the stream flow into zone 1) were not taken to be given by the $c_{source\ l}^{meas}$ values but, rather, allowed to vary as fitting parameters denoted $c_{source\ l}^{fit}$, the goal being to minimize ϕ_i^2 ; it was again assumed that no other sources were acting on the stream (or at least that if others were acting, their effects could be captured by adjusting the $c_{source\ l}^{fit}$ values).

The optimizations were carried out with a generalized reduced gradient method [24], as implemented in the routine LOADNLP and OPTIMIZE from the SOLVER.DLL nonlinear optimization package (Frontline Systems, Boulder, CO, USA). Table 4 compares the resulting $c_{source\ l}^{fit}$ values with the $c_{source\ l}^{meas}$ values for TCE and MTBE. For both compounds, the fitting lowered the ϕ_i^2 by degrees that are both large and highly significant (99.9% confidence level). The dashed lines in Figures 2a and 3a give c_w^{mod} versus distance with the use of the $c_{source\ l}^{fit}$ values; Figures 2c and 3c give the corresponding SA plots.

DISCUSSION

For TCE, the use of $c_{source\ l}^{meas}$ values leads to c_w^{mod} values that underpredict the measured c_w values for zones 4 through 10 (Fig. 2a). Thus, $c_{source\ l}^{fit}/c_{source\ l}^{meas} > 1$ for several of the downstream zones. Either some $c_{source\ l}^{meas}$ values were lower than the true volume averages for the groundwater input concentrations, or some unknown point sources were acting along the stream (or both). Given the multitude of sources that are known to exist in the general area of the study system, it is not surprising that some sources were underestimated or missed in the sampling that was conducted. Regarding zones 8c and 9, we note that weirs and spillways can substantially reduce stream supersaturation of a dissolved gas [10,25–27]. The essential absence of a reduction in the TCE concentration going from the upstream side of zone 8c to the upstream side of 9c thus suggests that some unknown source(s) could have been acting over zone 8c, although it remains possible that a random analytical error

of approximately $\pm 10\%$ could have masked a portion of the concentration decrease caused by the dam spillway at the 8c/9 boundary. Analogous comments pertain to the expected effects of the weir at the 9c/10 boundary.

When the SA results for TCE obtained by the $c_{source\ l}^{fit}$ values (Fig. 2c) are compared with those obtained by the $c_{source\ l}^{meas}$ values (Fig. 2b), an important similarity is the negligibility of the atmosphere as a source over the entire study section (α_{atm} remains very small). Second, in Figure 2b and c, the values of α_{inflow} , α_1 , and α_3 are greatly reduced by the time that the downstream end of the study section is reached: volatilization in the upper portion of the system reduces the overall concentration of TCE so that mass contributions from downstream sources can then substantially reduce the fractional SA importance of the upstream sources. The primary difference between Figure 2c relative to Figure 2b is the implication of four additional sources (specifically nonzero α_2 , α_8 , α_9 , and α_{10}).

For MTBE, use of the $c_{source\ l}^{meas}$ values leads to c_w^{mod} values that underpredict the measured c_w values for the upstream zones (Fig. 3a). Thus, $c_{source\ l}^{fit}/c_{source\ l}^{meas} > 1$ for several of the upstream zones. Either some $c_{source\ l}^{meas}$ values were lower than the true volume averages for the input groundwater concentrations, or some unknown point sources were acting along the stream (or both). Comments analogous to those made for TCE in this regard therefore apply here.

When the SA results for MTBE obtained with the $c_{source\ l}^{fit}$ values (Fig. 3c) are compared with those obtained with the $c_{source\ l}^{meas}$ values (Fig. 3b), an important similarity is an observable importance of α_{atm} . (Unlike the case for TCE, for MTBE, the degree of water/gas supersaturation is low enough that the invasive flux component is large enough relative to the c_w values to allow α_{atm} to reach observable values in SA plots.) A second similarity between Figure 3c and 3b involves the large reductions in α_{inflow} , α_1 , and α_3 achieved by the time the downstream end of the study section is reached: as with TCE, volatilization in the upper portion of the system reduces the overall concentration of MTBE so that mass additions in the downstream zones can substantially reduce the fractional SA importance of the upstream sources. The primary difference between Figure 3c and 3b is the implication of several additional sources, with important values of α_3 and α_5 in the mid-

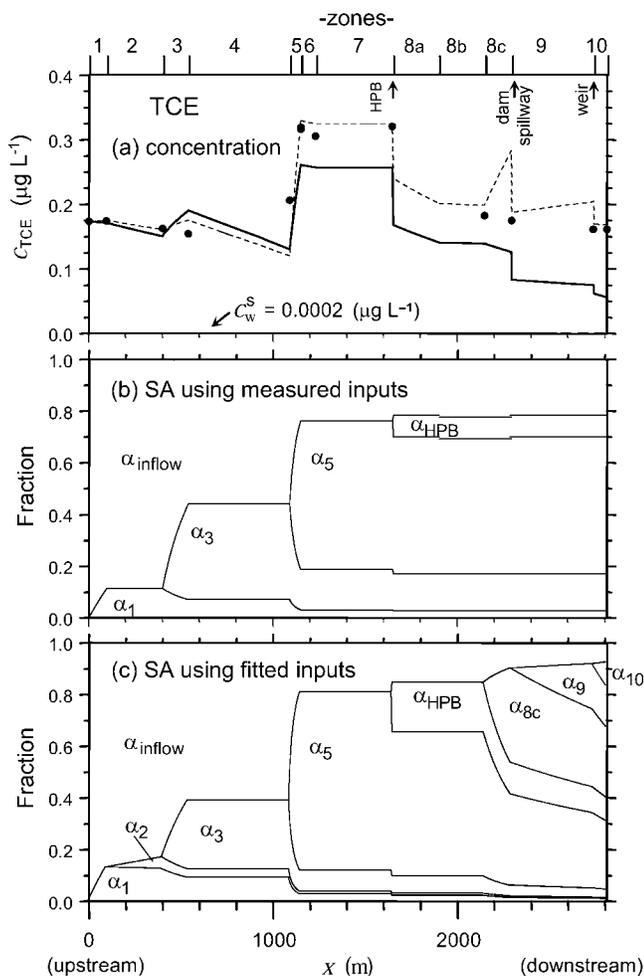


Fig. 2. Trichloroethene (TCE) in the Aberjona River (Massachusetts, USA). (a) Solid circles: measured concentrations (c_w). Straight dotted line (not visible): value of c_w^s for saturation equilibrium for dissolution of TCE from the measured atmospheric concentration. Solid line: modeled concentrations using the set of $c_{source\ i}^{meas}$ values and assuming no other sources. Dashed line: modeled concentrations using the set of $c_{source\ i}^{fit}$ values and assuming no other sources. (b) Source apportionment (SA) fractions predicted by the individual fluxes method and the set of $c_{source\ i}^{meas}$ values. (c) Source apportionment fractions predicted by the individual fluxes method and the set of $c_{source\ i}^{fit}$ values. HPB = Horn Pond Brook (Massachusetts, USA).

section and a large downstream value for α_9 . The existence of a source of MTBE (and TCE) in zone 5 is consistent with the observation of Asher et al. [11] that at least one unknown source in zone 5 contributes benzene, chloroform, 1,1-dichloroethane, *cis*-1,2-dichloroethene, and PCE to the river.

CONCLUSIONS

The results obtained here illustrate the utility of SA concepts when seeking to understand and identify sources and sinks causing the location- and time-dependent concentrations of contaminants in streams. Assuming good transverse mixing, the StreamVOC model uses well-understood parameterizations of volatilization to allow predictions of location-dependent SA allocations of VOC concentrations that will be limited in accuracy only by the accuracy of the input information on source locations, source concentrations, rates of inflow and outflow to and from the stream, etc. When input data on some relevant sources are missing, the model can be used to obtain best fit estimates of the locations and strengths of previously unknown

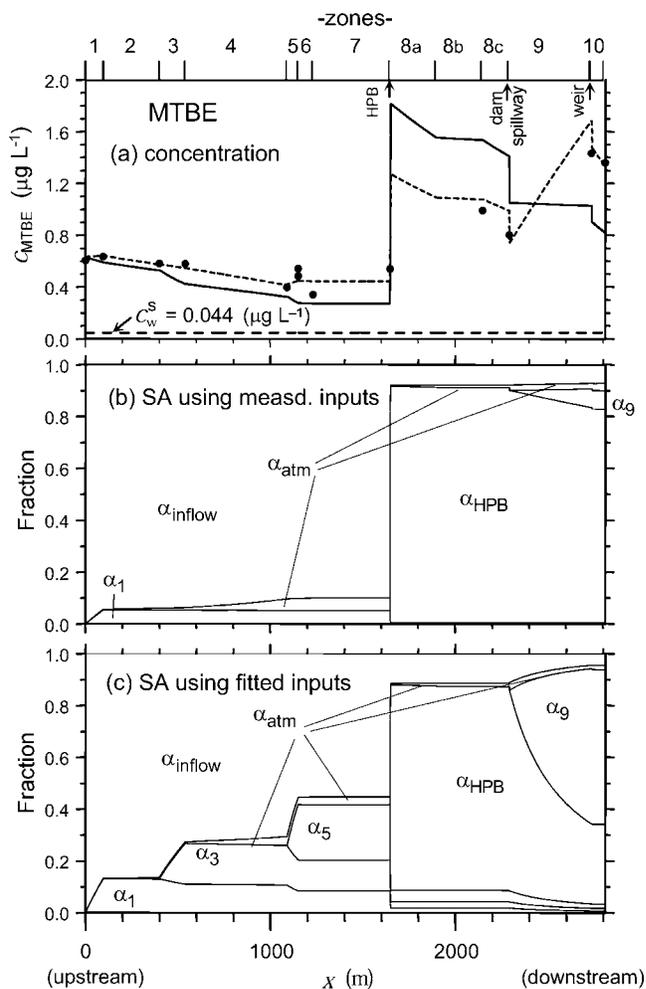


Fig. 3. Methyl-*tert*-butyl ether (MTBE) in the Aberjona River (Massachusetts, USA). (a) Solid circles: measured concentrations (c_w). Straight dotted line: value of c_w^s for the saturation equilibrium for dissolution of MTBE from the measured atmospheric level. Solid line: modeled concentrations using the set of $c_{source\ i}^{meas}$ values and assuming no other sources. Dashed line: modeled concentrations using the set of $c_{source\ i}^{fit}$ values and assuming no other sources. (b) Source apportionment (SA) fractions predicted by the individual fluxes method and the set of $c_{source\ i}^{meas}$ values. (c) Source apportionment fractions predicted by the individual fluxes method and the set of $c_{source\ i}^{fit}$ values. HPB = Horn Pond Brook (Massachusetts, USA).

sources. Even the relatively sparse data set obtained here was able to provide useful evidence for the likely locations and relative strengths of previously unknown sources in the Aberjona River.

Source apportionment modeling will be useful when considering strategies to reduce contaminant concentrations in streams. For example, on the basis simply of the stream data obtained for this work, it might have been assumed that re-

Table 3. Values of reduced least squares fit estimator (ϕ_i^2 , dimensionless) for trichloroethylene (TCE) and methyl-*tert*-butyl ether (MTBE); measure of the fit between measured and modeled c_w concentrations

| Compound | ϕ_i^2 Values for modeled c_w results | | ϕ_i^2 , ratio |
|----------|---|-----------------------|--------------------|
| | $c_{source\ i}^{meas}$ | $c_{source\ i}^{fit}$ | |
| TCE | 1.64 | 0.12 | 0.087 |
| MTBE | 1.55 | 0.21 | 0.14 |

Table 4. Measured and fitted source concentrations ($c_{\text{source } l}^{\text{meas}}$ and $c_{\text{source } l}^{\text{fit}}$, $\mu\text{g/L}$) for trichloroethylene (TCE) and methyl-*tert*-butyl ether (MTBE) with corresponding source strengths^a (g/d) for source flows to the Aberjona River (Massachusetts, USA)

| Source zone, <i>l</i> | TCE | | | | MTBE | | | |
|-----------------------|--|----------------|---|----------------|--|----------------|---|----------------|
| | Measured | | Fit | | Measured | | Fit | |
| | $c_{\text{source } l}^{\text{meas}}$ ($\mu\text{g/L}$) | Strength (g/d) | $c_{\text{source } l}^{\text{fit}}$ ($\mu\text{g/L}$) | Strength (g/d) | $c_{\text{source } l}^{\text{meas}}$ ($\mu\text{g/L}$) | Strength (g/d) | $c_{\text{source } l}^{\text{fit}}$ ($\mu\text{g/L}$) | Strength (g/d) |
| 1 | 0.21 | 0.67 | 0.25 | 0.79 | 0.34 | 1.1 | 0.90 | 2.9 |
| 2 | 0 | 0 | 0.14 | 0.27 | 0 | 0 | 0 | 0 |
| 3 | 0.39 | 3.1 | 0.26 | 2.1 | 0 | 0 | 0.47 | 3.8 |
| 5 | 1.09 | 5.1 | 1.65 | 7.7 | 0 | 0 | 0.69 | 3.2 |
| HPB ^b | 0.035 | 0.61 | 0.12 | 2.1 | 4.1 | 72 | 2.51 | 44 |
| 8c | 0 | 0 | 4.83 | 4.9 | 0 | 0 | 0 | 0 |
| 9 | 0 | 0 | 0.66 | 1.8 | 1.4 | 3.8 | 18.6 | 50 |
| 10 | 0 | 0 | 0.19 | 0.84 | 0 | 0 | 0 | 0 |

^a Calculated with ΔQ values from Table 1.

^b HPB = Horn Pond Brook (Massachusetts, USA). A source from Horn Pond Brook would operate similarly to a source for zone 8a. Therefore, in the fitting process, the latter was held at zero while the source strength for the former was adjusted.

duction of the TCE contamination entering in zone 5 would lead to a substantial reduction in the TCE contamination in zone 10. However, modeling based on minimization of ϕ_i^2 indicates that important sources of TCE likely exist downstream from zone 5; completely eliminating the TCE entering in zone 5 would result in a less than 50% reduction in the TCE concentration in zone 10. For MTBE, modeling based on minimization of ϕ_i^2 indicates that an important source of MTBE likely exists downstream from the confluence with HPB; completely eliminating the MTBE in HPB would result in a less than 50% reduction in the MTBE concentration in zone 10. Analogous considerations for other streams and rivers will be useful to water quality managers allocating limited resources for remediation and source control.

SUPPORTING INFORMATION

Supporting Information S1. Governing equations for streamVOC, physicochemical parameterizations used in streamVOC, and streamVOC model operation and numerical methods.

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