

## SOURCE APPORTIONMENT MODELING OF VOLATILE ORGANIC COMPOUNDS IN STREAMS

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**Abstract**—It often is of interest to understand the relative importance of the different sources contributing to the concentration  $c_w$  of a contaminant in a stream; the portions related to sources 1, 2, 3, etc. are denoted  $c_{w,1}$ ,  $c_{w,2}$ ,  $c_{w,3}$ , etc. Like  $c_w$ , the fractions  $\alpha_1 = c_{w,1}/c_w$ ,  $\alpha_2 = c_{w,2}/c_w$ ,  $\alpha_3 = c_{w,3}/c_w$ , etc. depend on location and time. Volatile organic compounds (VOCs) can undergo absorption from the atmosphere into stream water or loss from stream water to the atmosphere, causing complexities affecting the source apportionment (SA) of VOCs in streams. Two SA rules are elaborated. Rule 1: VOC entering a stream across the air/water interface exclusively is assigned to the atmospheric portion of  $c_w$ . Rule 2: VOC loss by volatilization, flow loss to groundwater, in-stream degradation, etc. is distributed over  $c_{w,1}$ ,  $c_{w,2}$ ,  $c_{w,3}$ , etc. in proportion to their corresponding  $\alpha$  values. How the two SA rules are applied, as well as the nature of the SA output for a given case, will depend on whether transport across the air/water interface is handled using the net flux  $F$  convention or using the individual fluxes  $J$  convention. Four hypothetical stream cases involving acetone, methyl-*tert*-butyl ether (MTBE), benzene, chloroform, and perchloroethylene (PCE) are considered. Acetone and MTBE are sufficiently water soluble from air for a domestic atmospheric source to be capable of yielding  $c_w$  values approaching the common water quality guideline range of 1 to 10  $\mu\text{g/L}$ . For most other VOCs, such levels cause net outgassing ( $F > 0$ ). When  $F > 0$  in a given section of stream, in the net flux convention, all of the  $\alpha_j$  for the compound remain unchanged over that section while  $c_w$  decreases. A characteristic time  $\tau_d$  can be calculated to predict when there will be differences between SA results obtained by the net flux convention versus the individual fluxes convention. Source apportionment modeling provides the framework necessary for comparing different strategies for mitigating contamination at points of interest along a stream.

**Keywords**—Source apportionment   Volatile organic compounds   Modeling   Volatilization   Henry's gas law

## INTRODUCTION

When a water sample obtained at a particular location and time  $t$  is found to contain a given contaminant at concentration  $c_w$ , there can be significant interest in understanding the identities and relative contributions of the different sources responsible for that concentration. Reasons for this type of source apportionment (SA) interest might involve the need to investigate the source(s) of previously unknown contamination, understand the identities and magnitudes of the important fate processes, and/or manage the total maximum daily load allocation of a stream among known sources.

Examples of SA efforts are available for groundwaters [1] and surface waters [2,3]. Our interest in SA applies to streams and watersheds (see Fig. 1). (The term stream here includes rivers.) This interest relates to the fact that the U.S. Geological Survey has been conducting analyses of stream samples for volatile organic compounds (VOCs), pesticides, nutrients, metals such as mercury, and wastewater contaminants at specific monitoring sites within various watersheds of the United States [4,5]. Of the various constituents that have been monitored, VOCs have been found to be some of the most frequently detected organic compounds found in water samples from urban streams and also have been found with significant frequency in the river source waters supplying 171 public water systems (Table 1). We seek here to improve the theoretical

framework that is available for understanding the SA aspects of those data.

The task of assigning  $(x, y, z, t)$ -dependent fractional SA values for VOCs in a given stream is characterized by special complexities. For example, a VOC present in a stream at a nonzero concentration  $c_w$  will tend to exchange with the atmosphere. If the VOC concentration in the atmosphere  $c_g$  is essentially zero over the entire stream reach of interest, there will be volatilization loss from the stream over the entire reach, and  $c_w$  will decline steadily. On the other hand, if  $c_g$  is not zero, but  $c_w$  is zero, then the stream can absorb some of the VOC from the atmosphere. Thus, a set of rules is needed for apportioning gains and losses of VOCs among the components of the total concentration that are assignable to the different operative sources. These rules will make it possible to specify, for any given point  $(x, y, z, t)$ , the fractions of an observed concentration that are due to each of the known sources for the stream, including the atmosphere.

## METHODS

*Basic source apportionment considerations*

When only a single source contributes a contaminant of interest to a watershed, then the SA of a given measured concentration obviously is trivial: 100% of the measured concentration in any sample is due to that single source. However, when multiple sources ( $j$ ) are involved, the SA modeling task is complicated by the need to consider the effects of the different source locations, source strengths, and loss processes

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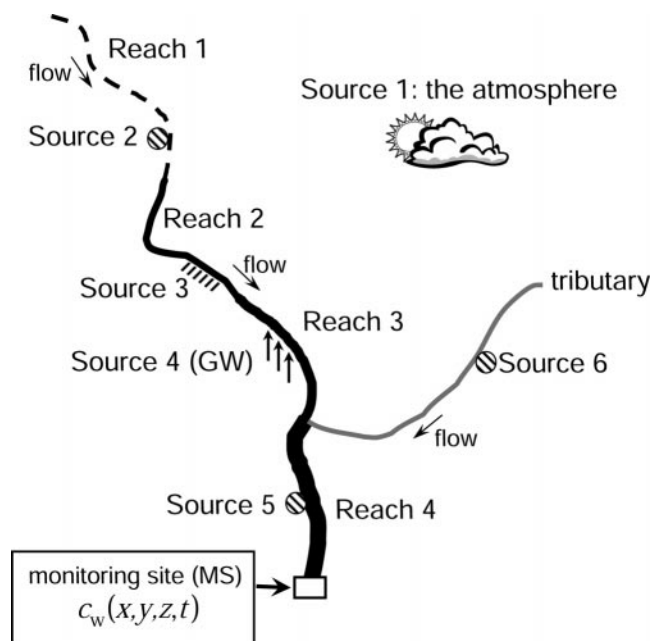


Fig. 1. Schematic representation of a portion of an example stream that is characterized by a series of four distinct hydrologic reaches (R1–R4). MS = monitoring site located at an  $x$ ,  $y$ ,  $z$  point and time  $t$  at which the contaminant concentration  $c_w(x, y, z, t)$  and the associated source apportionment (SA) are of particular interest (e.g., a water supply intake). The coordinate  $x$  is measured along the direction of flow. The coordinates  $y$  and  $z$ , which are measured transverse to the flow in the horizontal and vertical directions, are available for circumstances in which the stream is not mixed fully in the  $y$  and  $z$  directions along the entire stream length of interest. Six sources (S1–S6) of a contaminant of interest are shown: S1 is the atmosphere, which can contribute to the stream when the contaminant is present in the ambient air; S2 is a point source that inputs the contaminant at a single location within R1; S3 is a distributed (nonpoint) source within R2; S4 is a distributed source (arrows) associated with groundwater (GW) inflow over part or all of R3; and S5 is a point source in R4. The tributary inflow between R3 and R4 may introduce contaminant from another source (S6) and/or contaminant that originated in the ambient air (S1).

during the time ( $t$ ) that the contributions from each of the sources traveled in the water through space to a given point characterized by specific values of  $x$  (=distance downstream),  $y$  (=transverse horizontal coordinate), and  $z$  (=depth from the stream surface).

In any multisource case, a given total water concentration  $c_w(x, y, z, t)$  (with units  $\mu\text{g/L}$ ) may be comprised of specific contributions from sources 1, 2, 3, etc. in the watershed (see Fig. 1). The different contributions at  $(x, y, z, t)$  are denoted  $c_{w,1}(x, y, z, t)$ ,  $c_{w,2}(x, y, z, t)$ ,  $c_{w,3}(x, y, z, t)$ , etc. Because we will always be speaking of concentration in terms of a specific  $(x, y, z, t)$ , we hereafter drop that designation and write for each compound that

$$c_w = c_{w,1} + c_{w,2} + c_{w,3} + \dots = \sum_j c_{w,j} \quad (1)$$

It is assumed that the VOCs of interest here do not sorb to suspended or bed sediments: 100% of  $c_w$  is dissolved. This avoids the need to track compound mass that partitions to either suspended or bed sediments. In the atmosphere, VOCs are present essentially only in the gas phase: their particle-phase concentrations essentially are zero. It also will be assumed that the stream is well mixed both vertically and across the stream, so that each  $c_w$  is a function of just  $x$  and  $t$ .

Table 1. Detection frequency (%) of volatile organic compounds for water samples from 37 urban streams during 1996–2003<sup>a</sup> and from the river source waters for 171 public water systems (PWSs) during 1999 to 2000<sup>b</sup>

Compound	Detection frequency (% of samples analyzed)	
	Urban streams <sup>a</sup>	River source waters for 171 PWSs <sup>b</sup>
Toluene	76	3
Chloroform	56	16
Methyl- <i>t</i> -butyl ether	40	15
Trichloroethene	35	2
Perchloroethene	34	2
<i>cis</i> -1,2-Dichloroethene	34	<1
<i>m+p</i> -Xylene	28	<1
Benzene	23	<1
Chloromethane	15	<1
1,2,4-Trimethylbenzene	13	1
Methylene chloride	12	<1
1,1,1-Trichloroethane	11	<1
<i>o</i> -Xylene	11	<1
Bromodichloromethane	8.9	8
Ethylbenzene	7.0	<1
1,4-Dichlorobenzene	5.2	<1
Chlorodibromomethane	3.3	5
Styrene	3.2	<1
Methylethyl ketone (MEK)	1.3	5
Bromoform	1.2	1

<sup>a</sup> U.S. Geological Survey data for 37 urban streams from National Water Quality Assessment (NAWQA) Program Data Warehouse (<http://water.usgs.gov/nawqa/data>, accessed October 24, 2002). Data based on sampling each stream sampled six to 63 times during 1996–2003. Reporting levels of 0.02  $\mu\text{g/L}$  for all compounds except MEK (2  $\mu\text{g/L}$ ).

<sup>b</sup> Grady [34]. Reporting level: 0.2  $\mu\text{g/L}$  for all compounds except MEK (2.0  $\mu\text{g/L}$ ).

The fractional SA contributions of the various sources  $j$  to  $c_w$  are given by the location- and time-dependent fractional factors  $\alpha_j$  according to

$$\alpha_1 \equiv \frac{c_{w,1}}{c_w}, \quad \alpha_2 \equiv \frac{c_{w,2}}{c_w}, \quad \alpha_3 \equiv \frac{c_{w,3}}{c_w}, \quad \text{etc.} \quad (2)$$

For example, if source 1 is the atmosphere and source 2 is a leak near the stream, then  $\alpha_1$  and  $\alpha_2$  may be further identified as  $\alpha_{\text{atm}}$  and  $\alpha_{\text{leak}}$ . All of the  $\alpha_j$  depend on location and time because: the point and nonpoint sources in a watershed are associated with specific locations; source strengths usually vary with time; and loss processes usually are location- and time-dependent. Examples of point sources include municipal and industrial outfalls, in-stream or near-stream spills, runoff culverts, and narrow groundwater plumes that enter the stream. Nonpoint sources introduce contaminants over extended stream sections, and examples include overland runoff and wide zones of contaminated groundwater that enter the stream, and at the largest scale, the regional atmosphere. The approach indicated in Figure 2 can be used to plot SA results versus  $x$ .

The SA approaches that have been utilized for streams are of two basic types. Deductive/retrospective approaches solve some type of inverse problem by using chemical analysis results from field samples alone (as in cluster, principal component, and factor analyses), or from compound-specific source profiles that can be combined mathematically in search of the SA that best matches the field sample profile(s) of interest (as in source-receptor modeling). Predictive/prospective

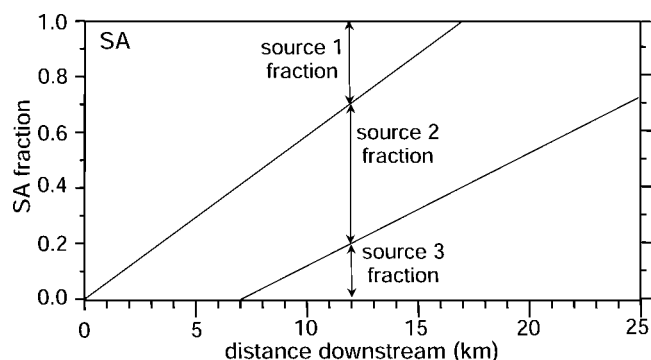


Fig. 2. Example stream source apportionment (SA) values for three sources as a function of distance for the first 25 km of a stream. At  $x = 12$  km,  $\alpha_1 = 0.3$ ,  $\alpha_2 = 0.5$ , and  $\alpha_3 = 0.2$ .

approaches utilize knowledge of the operative hydrology together with knowledge of the characteristics of the important sources (chemical profiles, strengths, location, etc.) to predict  $c_w$  deterministically as a function of  $(x, y, z, t)$ .

Applications of deductive/retrospective SA models to natural water systems include the cluster/principal components analysis of river basin monitoring data by Simeonov et al. [6,7]; the factor analysis of trace metals in streams by Pekey et al. [8]; the cluster/principal components analysis of water quality data by Nikolov et al. [9]; and the source-receptor modeling of polycyclic aromatic hydrocarbons (PAHs) in sediments by Singh et al. [10], Sharma et al. [11], and Li et al. [12], polychlorinated dibenzodioxins and dibenzofurans (PDD/Fs) in sediments by Su and Christensen [13], sulfate by Eatough et al. [14], and total loads of sediment mass by Kelley and Nater [15,16]. Applications of predictive/prospective SA models to natural water systems include considerations of the sources of chemical oxygen demand in a watershed [17] and nutrient modeling [3,18].

Hybrid SA approaches that utilize both deductive and predictive elements offer great promise as research tools. For example, field sample analytical data from a monitoring site of interest can be combined with a knowledge of the corresponding hydrology to back out probable source locations and strengths, as well as SA assignments downstream of the monitoring site (e.g., [2,19–22]). In current practice, because of the ease with which computer model parameters can be adjusted and models rerun, most SA modeling is likely to take place in the hybrid mode. The approach described here can be used in a deductive mode, a predictive mode, or in hybrid mode.

#### Henry's gas law partitioning

Equilibrium Henry's gas law (HGL) partitioning between air and water is described by

$$\frac{c_g}{c_w^s} = \frac{H}{RT} \quad (3)$$

where  $c_g$  ( $\mu\text{g/L}$ ) is the air concentration of a compound of interest,  $c_w^s$  ( $\mu\text{g/L}$ ) is the equilibrium saturation value of the water concentration  $c_w$  that corresponds to that  $c_g$ , the parameter  $H$  ( $\text{m}^3 - \text{Pa/mol}$ ) is the compound- and temperature-dependent HGL constant,  $R$  is the gas constant ( $8.314 \text{ m}^3 - \text{Pa/K-mol}$ ), and  $T$  is temperature (K). Note that, unlike the water solubility limit for the  $T$  of interest, there is no single value of  $c_w^s$ : As  $c_g$  increases, so too does  $c_w^s$ . (The upper limit on  $c_g$

is the saturation vapor pressure of the pure liquid compound.) The examples considered in this paper will assume a constant value of  $T$  and thus a constant value of  $H$  for each compound of interest. In the general case, however, the effects of diurnal and longer term variations in  $T$  will need to be considered.

#### The net flux $F$

At point  $(x, t)$ , the net flux  $F$  ( $\mu\text{g/m}^2 - \text{s}$ ) from air into the stream at  $z = 0$  can be parameterized using the first-order rate law (e.g., see [23,24])

$$F = (10^3 \text{ L/m}^3)k_{\text{OL}}(c_w^s - c_w) \quad (4)$$

where the overall gas/liquid transfer velocity  $k_{\text{OL}}$  (m/s) depends on the flow conditions in the stream, the air and water temperatures, wind speed, and the molecular properties of the compound. When  $F > 0$ , there is net deposition of the compound, and the atmosphere is acting as a source; when  $F < 0$ , there is net volatilization loss of the compound to the atmosphere. When  $F = 0$ , then there is equilibrium between the water and the atmosphere, and no net flux. However, even when  $F = 0$ , there still is exchange between the compartments whenever  $c_g \neq 0$ .

#### The individual fluxes $J_{\text{abs}}$ and $J_{\text{vol}}$

For each gaseous atmospheric constituent, there is constant molecular impingement on the water surface ( $z = 0$ ): some fraction of the impinging molecules always will be absorbed into the water and then transferred by molecular and turbulent diffusion into the underlying bulk water. This remains true even when there is net volatilization of the compound from the water to the atmosphere. Conversely, in the water phase, some of the molecules of the compound of interest always will be volatilizing to the gas phase, even when there is net deposition from the atmosphere to the water. The needed expressions may be found within Equation 4. For the instantaneous absorption flux at  $z = 0$

$$J_{\text{abs}} = (10^3 \text{ L/m}^3)k_{\text{OL}}c_w^s \quad (5)$$

For the instantaneous volatilization flux at  $z = 0$

$$J_{\text{vol}} = (10^3 \text{ L/m}^3)k_{\text{OL}}c_w \quad (6)$$

For the next flux,

$$F = J_{\text{abs}} - J_{\text{vol}} = (10^3 \text{ L/m}^3)k_{\text{OL}}(c_w^s - c_w) \quad (7)$$

Equations 5 to 7 have been utilized in other gas-transfer studies (e.g., [25]).

#### SA conventions for volatilizable compounds

*The  $SA_F$  net flux convention.*  $F$  and  $J_{\text{abs}}$  generally will take on very different values in any given circumstance. This means that there are two possible conventions for when to count inputs from the atmosphere in SA calculations. In the  $SA_F$  convention, only the net flux  $F$  is considered: compound mass is only considered as added to the stream from the atmosphere for SA calculations when  $F > 0$  and only removed to the atmosphere when  $F < 0$ .

*The  $SA_J$  individual flux convention.* In the  $SA_J$  convention, compound mass is added to the stream from the atmosphere for SA calculations whenever  $J_{\text{abs}} > 0$  and removed whenever  $J_{\text{vol}} > 0$ . When applying the  $SA_J$  convention, it usually is convenient to assume that the mass of the exchanging compound in the atmosphere is large relative to what is found in the stream: compound lost from the stream neither affects  $c_g$

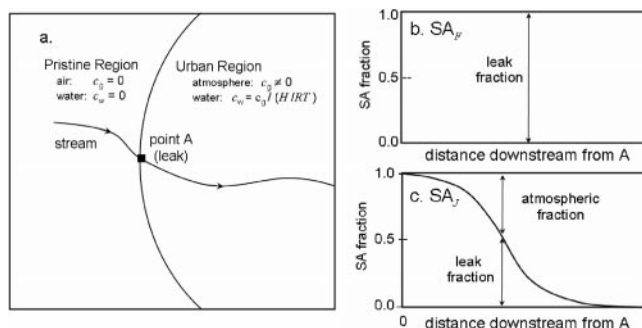


Fig. 3. (a) Assumed physical characteristics of a hypothetical model stream that passes first through a pristine region and then into an urban region in which the air concentration  $c_g$  of a contaminant of interest is nonzero. A subsurface leak located at point A on the boundary of the urban region leads to a water concentration of the contaminant that by coincidence is equal to the equilibrium value that would be specified by  $c_g$  in the urban region. (b) Source apportionment (SA) results by the  $SA_F$  convention. (c) SA results by the  $SA_J$  convention.

nor requires further tracking as it becomes part of the atmospheric reservoir of the compound.

*Comparison of the  $SA_F$  and  $SA_J$  conventions using a simple hypothetical example.* The  $SA_F$  and  $SA_J$  approaches can lead to very different SA results for a volatilizable compound. Some important consequences of the differences between the two approaches can be exemplified by consideration of the following simple hypothetical example (see Fig. 3). A stream originates in a pristine region and flows with constant discharge for its entire, extended length. We suppose that a compound called X is absent completely from both the atmosphere and the stream throughout the pristine region. At point A: The stream leaves the pristine region; enters (and subsequently remains in) an urban zone throughout which X is present in the urban air at a constant, nonzero  $c_g$ ; has had zero time to absorb X from the nonzero  $c_g$ ; immediately is affected by an underground leak of X that abruptly causes  $c_w$  in the stream to rise from 0 to a value that, by coincidence, equals  $c_g/(H/[RT])$ . Note that because  $c_g/(H/[RT])$  is the equilibrium water concentration  $c_w^s$  specified by  $c_g$ , then downstream of point A we have  $F = 0$  for compound X. These conditions are summarized in Appendix 1.

In the pristine region,  $c_w = 0$ , and no SA calculations are required. In the urban region, the implications of each of the two SA conventions may be understood as follows. In the  $SA_F$  convention, because  $F = 0$  throughout the urban region,  $\alpha_{\text{atm}} = 0$  throughout that zone. And, because the hypothesized leak is the only source that affects  $c_w$  in the stream,  $\alpha_{\text{leak}} = 1$  throughout the urban region (Fig. 3b). In the  $SA_J$  convention,  $\alpha_{\text{leak}} = 1$  at point A. However, downstream of A, because  $J_{\text{abs}} > 0$ , the fraction of X in the stream that originated from the leak begins to be diminished by an influx of atmospheric X. At the same time, because  $J_{\text{vol}} > 0$ , leak-related molecules of X volatilize to the atmosphere. The result in the  $SA_J$  convention is that, if the stream continues to flow under these conditions for a long distance, then eventually  $\alpha_{\text{leak}} \rightarrow 0$  and  $\alpha_{\text{atm}} \rightarrow 1$  (Fig. 3c).

The  $SA_F$  convention represents the strictest possible interpretation of SA responsibilities for land-based sources: the fact that a contaminant released to the aquatic environment has exchanged with the atmosphere grants no dispensation to the responsible party. After all, any atmospheric contamination that is available for exchange with the stream is the direct

consequence of land-based sources such as the source at point A in Figure 3. On the other hand, from a scientific viewpoint, the  $SA_J$  convention recognizes the role that the atmosphere plays as a source, including the immediate origins of the mix of specific molecules making up a given stream concentration  $c_w$ .

#### Source apportionment rules for volatilizable compounds

*General SA rules.* When some source  $j$  contributes differential mass  $dm_j > 0$  of the compound of interest to a volume element  $V$  of stream water, then all of that mass is assigned to  $c_{w,j}$  so that

$$\frac{dc_{w,j}}{dt} = \frac{1}{V} \frac{dm_j}{dt} \quad \text{SA rule 1: Allocating an addition from a source } j \quad (8)$$

where, for the sake of mathematical simplicity, we are assuming zero local changes in the stream discharge, no loss processes operating on  $c_w$ , and complete transverse mixing over the average local stream width  $w$  and depth  $h$ .

When a loss process is operating so that  $dm < 0$  (e.g., volatilization to the atmosphere, degradation, or flow loss to groundwater), the loss must be distributed over all the different components of  $c_w$ . Because the individual molecules making up the components  $c_{w,1}$ ,  $c_{w,2}$ ,  $c_{w,3}$ , etc. are perfectly equivalent at the molecular level, the loss will be distributed proportionally across all of the components according to the local values of the fractions  $\alpha_j$ . Thus, for each  $j$ , we have

$$\frac{dc_{w,j}}{dt} = \alpha_j \frac{1}{V} \frac{dm}{dt} \quad \text{SA rule 2: Allocating any loss } (dm < 0) \text{ among all } j \quad (9)$$

where it is understood that the  $\alpha_j$  are functions of location and time, and we assume zero local changes in the stream discharge, and complete transverse mixing over the average local stream width and depth.

*Application of the general SA rules to atmospheric exchange in the  $SA_F$  convention.* For net absorption from the atmosphere such that  $F > 0$ , and with  $j$  specifically corresponding to the atmospheric source ( $j = \text{atm}$ ), then application of SA rule 1 in the  $SA_F$  convention yields

$$\frac{dc_{w,\text{atm}}}{dt} = \frac{F}{h} \quad j = \text{atm: } SA_F \text{ application of SA rule 1 for addition from the atmosphere} \quad (10)$$

where an average stream depth of  $h$  has been assumed. Equation 10 prescribes that, when the stream is gaining mass of the compound of interest from the atmosphere ( $F > 0$ ), 100% of  $F$  is assigned to  $c_{w,\text{atm}}$ , the atmospheric-related component of  $c_w$ .

For net loss by volatilization to the atmosphere such that  $F < 0$ , application of SA rule 2 in the  $SA_F$  convention yields for each and every  $j$  (including  $j = \text{atm}$ ) that

$$\frac{dc_{w,j}}{dt} = \alpha_j \frac{F}{h} \quad \text{for all } j: SA_F \text{ application of SA rule 2 for loss by volatilization to the atmosphere} \quad (11)$$

*Application to atmospheric exchange in the  $SA_J$  convention.* For exchange with the atmosphere, we first consider when  $j$  specifically corresponds to the atmospheric source ( $j = \text{atm}$ ). The  $SA_J$  convention in this case yields

$$\frac{dc_{w,\text{atm}}}{dt} = \frac{J_{\text{abs}}}{h} - \alpha_j \frac{J_{\text{vol}}}{h} \quad \text{for } j = \text{atm: } SA_J \text{ application of SA rule 1 and SA rule 2 for atmospheric exchange} \quad (12)$$

where the first term on the right-hand side reflects application of SA rule 1 and the second term reflects application of SA rule 2. In the SA<sub>j</sub> convention, the component  $c_{w,atm}$  thus is affected simultaneously by both  $J_{abs}$  and  $J_{vol}$ , even when  $F = 0$ .

For exchange with the atmosphere, for all  $j \neq atm$ , application of SA rule 2 in the SA<sub>j</sub> convention yields

$$\frac{dc_{w,j}}{dt} = -\alpha_j \frac{J_{vol}}{h} \quad \text{for all } j \neq atm: \text{ SA}_j \text{ application of SA rule 2}$$

for loss to the atmosphere (13)

The minus signs in the terms involving  $J_{vol}$  in Equations 12 and 13 are required because the loss rate  $J_{vol}$  is defined such that  $J_{vol} \geq 0$ . Note that, although Equation 13 applies for all  $j$  except the atmospheric source,  $-\alpha_j J_{vol}/h$  also applies to  $dc_{w,j}/dt$  for  $j = atm$ , but along with an additional term so that a separate equation is required (see Eqn. 12).

*Application to nonvolatilization losses in both the SA<sub>F</sub> and SA<sub>j</sub> conventions.* The SA<sub>F</sub> and SA<sub>j</sub> conventions differ in how they treat movement of mass across the air/water interface, but not in any other way. Treatment of nonvolatilization losses (e.g., degradation, flow loss to groundwater, etc.) thus is the same in both conventions.

For loss by degradation, a first-order rate law of the type  $dc_w/dt = -k_{deg}c_w$  usually is assumed (e.g., see [25]). Although a more complex rate expression can underlie the operative kinetics, usually the information needed to implement a more complex rate law is not available. Moreover, although in a stream modeling effort it is possible that more than one type of degradation mechanism may be acting to remove a compound (e.g., biodegradation, abiotic hydrolysis, etc.), in most cases there will not be enough information available to invoke anything more complex than a single mechanism-averaged degradation rate constant  $k_{deg}$  (d<sup>-1</sup>) with

$$\frac{dc_w}{dt} = -k_{deg}c_w \quad (14)$$

so that

$$\frac{dc_{w,j}}{dt} = -\alpha_j k_{deg}c_w \quad \text{for all } j: \text{ Loss by degradation. Application of SA rule 2 (applies to both SA}_F \text{ and SA}_j \text{ conventions)} \quad (15)$$

The same assumptions invoked for the simplified representation of Equation 8 apply here as well. Note that values for  $k_{deg}$  are very dependent on compound, temperature, and the nature of the system; for a given compound and temperature,  $k_{deg}$  values easily can vary by over two orders of magnitude among different types of natural water systems.

When a section of stream loses water by infiltration to groundwater, a dissolved compound will be carried out of the stream by the recharge flow. As with Equation 15, the loss will be distributed over all  $j$  according to the  $\alpha_j$  values. We note here that, if none of the lost water ever reenters the stream, then no further consideration is required for the lost mass. However, if some of the water that leaves the stream reenters at some downstream point, then it will become necessary to track the components of the concentration within the associated groundwater flow paths so that proper reallocations to the stream  $c_{w,j}$  values can be made as the flow paths emerge from the stream bottom. Similarly, strictly speaking, the components of the VOC mass lost from the stream to the atmosphere would need to be tracked in a coupled stream/air-shed model. In most cases, however, a single stream will not be capable of affecting

the local air-shed concentration of a compound of interest, and so the mass entering the atmosphere will not require further consideration. Appendix 2 summarizes the allocation features of the SA<sub>F</sub> and SA<sub>j</sub> approaches.

*The characteristic time  $\tau_a$  and the characteristic distance  $\lambda_{km}$  for  $J_{abs}$  to alter nonatmospheric  $\alpha$  values in the SA<sub>j</sub> convention*

Given an initial stream concentration  $c_w$  of some compound of interest, the flux rate  $J_{abs}$  may or may not be large enough to add enough molecules to affect the makeup of  $c_w$  within the flow times of interest. The relevance of this question may be understood by consideration of an example stream system that is similar to that in Figure 3a in all ways except that  $c_w$  is not necessarily equal to  $c_g/(H/RT)$ . For such a stream, the magnitude of  $J_{abs}$  may or may not be large enough to alter the condition  $\alpha_{leak} \approx 1$  in the SA<sub>j</sub> convention to any significant degree within the flow time of interest. The  $\alpha$  plot in Figure 3c applies to a case where  $J_{abs}$  is large enough to accomplish this. This certainly will not be the case in all situations, particularly when dealing with high  $c_w/c_w^s$  ratios, deep streams (i.e., large  $h$ ), and slow-moving streams (small  $k_{OL}$ ). The roles of each of these three parameters may be understood as follows.

Assuming a constant average depth  $h$  (m) and a constant average width  $w$  (m), then

$$\begin{aligned} (10^3 \text{ L/m}^3) \times c_w \times wh \\ = \text{mass in stream per unit length of stream} \\ \text{units: } \frac{\mu\text{g}}{\text{m}} \end{aligned} \quad (16)$$

and

$$\begin{aligned} J_{abs}w = \text{mass per unit time entering stream from atm. per} \\ \text{unit length of stream} \\ \text{units: } \frac{\mu\text{g}}{\text{s} - \text{m}} \end{aligned} \quad (17)$$

By combination of Equations 16 and 17, we find the important ratio

$$\begin{aligned} \frac{(10^3 \text{ L/m}^3)c_w wh}{J_{abs}w} \\ = \frac{(10^3 \text{ L/m}^3)c_w h}{J_{abs}} = \tau_s(x) \\ = (\text{mass in stream per unit length of stream}) \\ \div (\text{mass per unit time entering stream from atm. per} \\ \text{unit length of stream}) \\ \left( \text{units: } \frac{\frac{\mu\text{g}}{\text{m}}}{\frac{\mu\text{g}}{\text{s} - \text{m}}} = \text{s} \right) \end{aligned} \quad (18)$$

As indicated, the group  $\tau_s(x) = (10^3 \text{ L/m}^3)c_w h/J_{abs}$  has units of s. It represents the minimum possible time that would be required for  $J_{abs}$  to replace all of the mass of the compound found at  $x$  in a full, top-to-bottom vertical element of the stream (assuming no downstream changes in the stream characteristics and no subsequent sources). Substituting for  $J_{abs}$  by Equation 5, we obtain

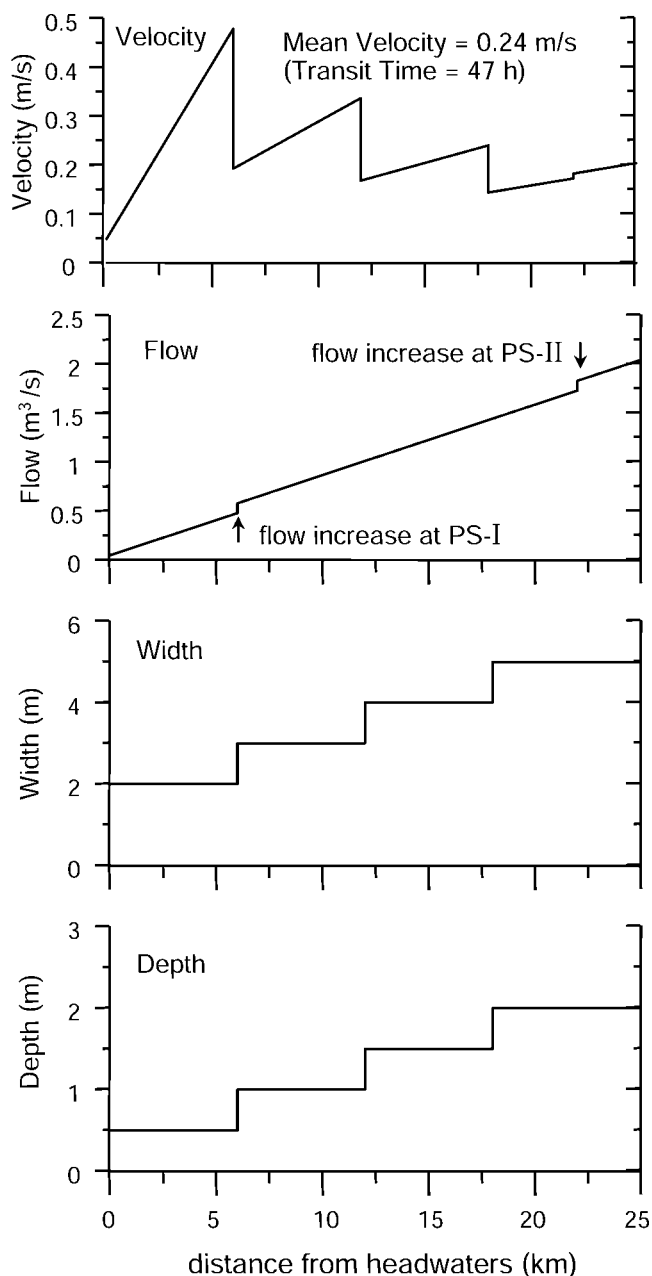


Fig. 4. Assumed functionalities for stream velocity ( $u$ ), flow ( $Q$ ), width ( $w$ ), and depth ( $h$ ) for cases 1–4. PS = point source.

$$\tau_s(s) = \frac{c_w h}{c_w^s k_{OL}} \quad (\text{units: s}) \quad (19)$$

$$= \frac{c_w}{c_g/(H/RT)} \frac{h}{k_{OL}} \quad (\text{units: s}) \quad (20)$$

The RHS of Equation 19 embodies each of the three controlling parameters discussed above, namely  $c_w/c_w^s$ ,  $h$ , and  $k_{OL}$ . For units of days (d), we have

$$\tau_d(x) = \frac{c_w h}{c_w^s k_{OL}} \times \left( \frac{1 \text{ d}}{86,400 \text{ s}} \right) \quad (\text{units: d}) \quad (21)$$

$$= \frac{c_w}{c_g/(H/RT)} \frac{h}{k_{OL}} \times \left( \frac{1 \text{ d}}{86,400 \text{ s}} \right) \quad (\text{units: d}) \quad (22)$$

Equations 20 and 22 are obtained by expansion of  $c_w^s$ . When

the stream is flowing at an average velocity  $\bar{u}$  (m/s), then the distance parameter  $\lambda_{km}(x)$  that corresponds to  $\tau_s$  is

$$\lambda_{km}(x) = \bar{u} \tau_s(x) \times \left( \frac{1 \text{ km}}{1000 \text{ m}} \right) \quad (\text{units: km}) \quad (23)$$

As noted,  $\tau_s(x)$ ,  $\tau_d(x)$ , and  $\lambda_{km}(x)$  are all functions of  $x$ .

#### Example cases

Four example cases are considered to illustrate the SA principles discussed above for VOCs in streams. The simulations were carried out in a predictive (deterministic) manner using the numerical SA model STREAMVOC.1 [26] with modifications that allow both  $SA_F$  and  $SA_J$  calculations. The input values for the variables describing the assumed stream system and sources are summarized in Appendix 3 and Figure 4. Highly simplified inputs were assumed for the system parameters, e.g., stream flow, width, and depth; air and water temperature; etc. Although SA modeling certainly can take place with complex functionalities for those parameters, simple inputs are adequate when illustrating SA principles governing VOCs in streams.

Not all of the possible stream characteristics depicted in Figure 1 are represented in the basic system shared by the four cases. For example, in Figure 1, the possibility of stream flow loss to groundwater is depicted in the upper reaches of the stream, while, in all of the four example cases, it is assumed that groundwater is providing flow into the stream over the entire 25-km modeled length of the stream.

The atmospheric concentrations selected for case 1 (methyl-*tert*-butyl ether [MTBE], 0.026  $\mu\text{g/L}$ ; acetone, 0.14  $\mu\text{g/L}$ ), case 2 (chloroform, 0.0018  $\mu\text{g/L}$ ), case 3 (MTBE, 0.026  $\mu\text{g/L}$ ; benzene, 0.009  $\mu\text{g/L}$ ), and case 4 (PCE, 0.0035  $\mu\text{g/L}$ ) represent values from within the upper ranges that have been measured by Pankow et al. [27] in urban air of the United States. For HGL saturation equilibrium at 25°C between water and these air concentrations, the aqueous  $c_w^s$  values for MTBE, acetone, chloroform, benzene, and PCE are 0.95, 67, 0.011, 0.041, and 0.0056  $\mu\text{g/L}$ , respectively (Appendix 3).

Although relatively few degradation rate data are available for VOCs, Rathbun [23] provides a careful review of considerable relevant data for both aerobic and anaerobic conditions. Of the five compounds considered here, acetone and benzene are the most biodegradable. Aerobically, for acetone,  $k_{deg}$  values as high as 0.9  $\text{d}^{-1}$  have been observed [28], though in simulated streams considerably slower degradation also has been observed [29–32]. Degradation of acetone is not considered in case 1 in order that we can examine the full potential of urban air for introducing this highly water-soluble compound into surface waters. For benzene, Rathbun [23] reports a range of 0.043 to 0.14  $\text{d}^{-1}$  for aerobic conditions. In preliminary calculations performed for this work, it was observed that  $k_{deg} = 0.14 \text{ d}^{-1}$  was not large enough to cause much noticeable effect on either  $c_w(x)$  or its SA allocations for the modeled stream. However, when  $k_{deg}$  for benzene was assigned a three times larger value ( $=0.43 \text{ d}^{-1}$ ), the effects of degradation became easily noticeable in the SA model output and so that value was chosen for case 3. The compounds MTBE, chloroform, and PCE are minimally degradable on the time-scale of days, and so degradation of those compounds is neglected in cases 2 to 4.

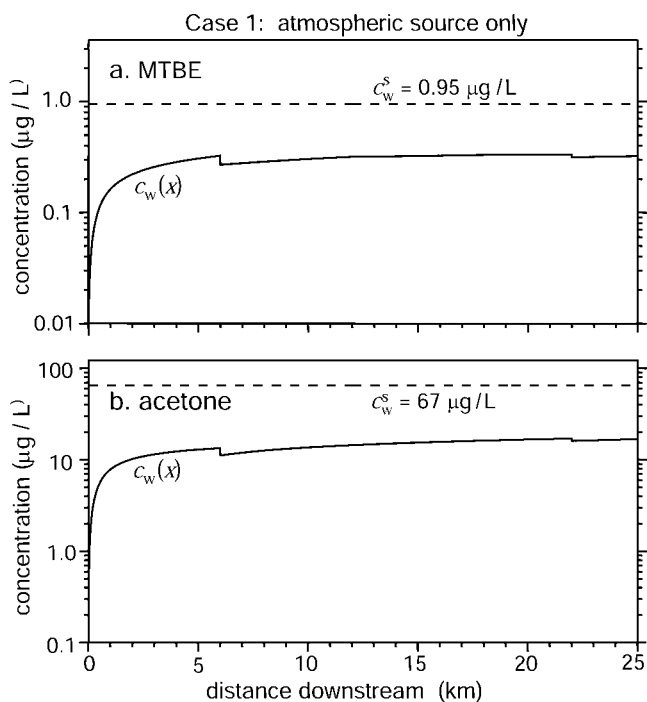


Fig. 5. Stream concentration  $c_w(x)$  values for case 1. (a) Methyl-*tert*-butyl ether (MTBE) in the atmosphere at  $0.026 \mu\text{g/L}$ . No other sources. (b) Acetone in the atmosphere at  $0.14 \mu\text{g/L}$ . No other sources. Ambient temperature =  $25^\circ\text{C}$ . Other conditions as given in Figure 4 and Appendix 3.

## RESULTS

### Case 1—Atmospheric source of MTBE and acetone ( $SA_F$ and $SA_J$ results are equivalent for all $x$ )

The results for case 1 for MTBE and acetone are presented in Figure 5. The atmosphere is the only source in this case and so it accounts for 100% of each  $c_w(x)$  value as  $c_w(x)$  increases down the length of the flow. We reiterate that we are assuming complete transverse  $y$ ,  $z$  mixing, a steady state water flow regime, and a uniform  $c_g \neq 0$  atmospheric source. With the atmosphere as the only source, there are no differences between the  $SA_F$  and  $SA_J$  approaches.

For the stream dynamics considered here, neither MTBE nor acetone is able to approach equilibrium with the atmosphere (so that  $c_w(x) = c_w^s$ ) at any point in the stream. The fact that  $c_w(x)$  for MTBE and acetone do approach relatively constant values of approximately 0.3 and  $15 \mu\text{g/L}$ , respectively, by  $x \approx 5 \text{ km}$  indicates an approach to steady state between the opposing influences of VOC mass addition by ingassing from the atmosphere and the rate at which VOC-free dilution water is entering the stream from the groundwater zone. The ratios of these steady concentrations to their corresponding  $c_w^s$  values are approximately  $0.3/0.95 = 0.32$  (MTBE) and approximately  $15/67 = 0.22$  (acetone). The lower ratio for acetone is due to its significantly lower  $H$  value as compared to MTBE, which causes its  $k_{OL}$  values for the stream to be generally smaller than those for MTBE (see Appendix 3, item 1.i) because of some air-side resistance to air/water mass transfer. The two concentration and stream flow discontinuities at river km values of 6 and 22 km are the result of the inflows of VOC-free effluent from point source I (PS-I) and from point source II (PS-II).

Of the compounds considered in the four example cases, MTBE and acetone by far are the most water soluble from air

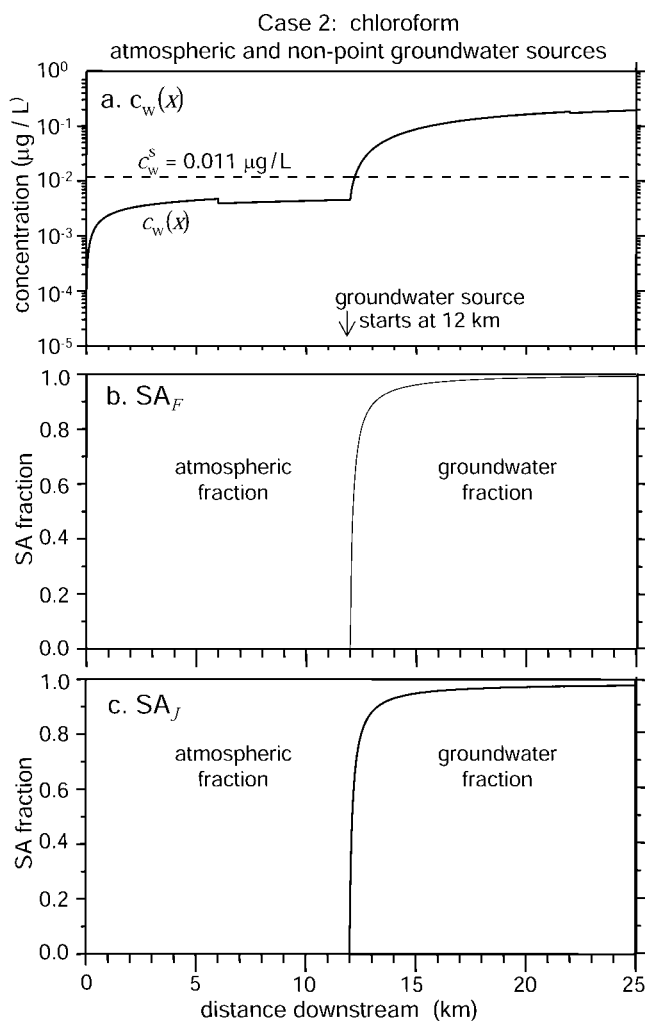


Fig. 6. (a) Stream concentration  $c_w(x)$ , (b) source apportionment ( $SA_F$ ), and (c) source apportionment  $SA_J$  versus distance for chloroform in case 2. Chloroform in the atmosphere at  $0.0019 \mu\text{g/L}$ , and chloroform at  $0.5 \mu\text{g/L}$  in the groundwater entering the stream from  $x = 12$  to  $25 \text{ km}$ . Ambient temperature =  $25^\circ\text{C}$ . Other conditions as given in Figure 4 and Appendix 3.

(lowest  $H/RT$  values). As a result, these are the only compounds for which the ambient air concentrations considered here are capable of yielding stream concentrations that approach the types of limits frequently discussed in a regulatory context (i.e., approximately 1 to  $10 \mu\text{g/L}$ ). As will be seen below, the compounds chloroform, benzene, and PCE are too volatile (i.e.,  $H/RT$  too large) for atmospheric levels to yield significant stream concentrations (see also Appendix 3, item 1.h).

### Case 2—Atmospheric and groundwater sources of chloroform

The case 2 results are presented in Figure 6.  $SA_F$  and  $SA_J$  results are equivalent for  $x < 12 \text{ km}$ , and observably different for  $x > 12 \text{ km}$ . Over the first 12 km of the stream, the atmosphere is the only source of chloroform in the stream. Thus, as  $c_w(x)$  increases over  $x = 0$  to  $12 \text{ km}$  (Fig. 6a), the atmosphere accounts for 100% of each  $c_w(x)$  value in both the  $SA_F$  and  $SA_J$  conventions. In that region, as with MTBE and acetone in case 1, the stream-level of chloroform does not approach equilibrium with the atmosphere, but does approach a relatively steady value ( $\sim 0.004 \mu\text{g/L}$ ) by  $x \approx 5 \text{ km}$ . For  $x > 12$

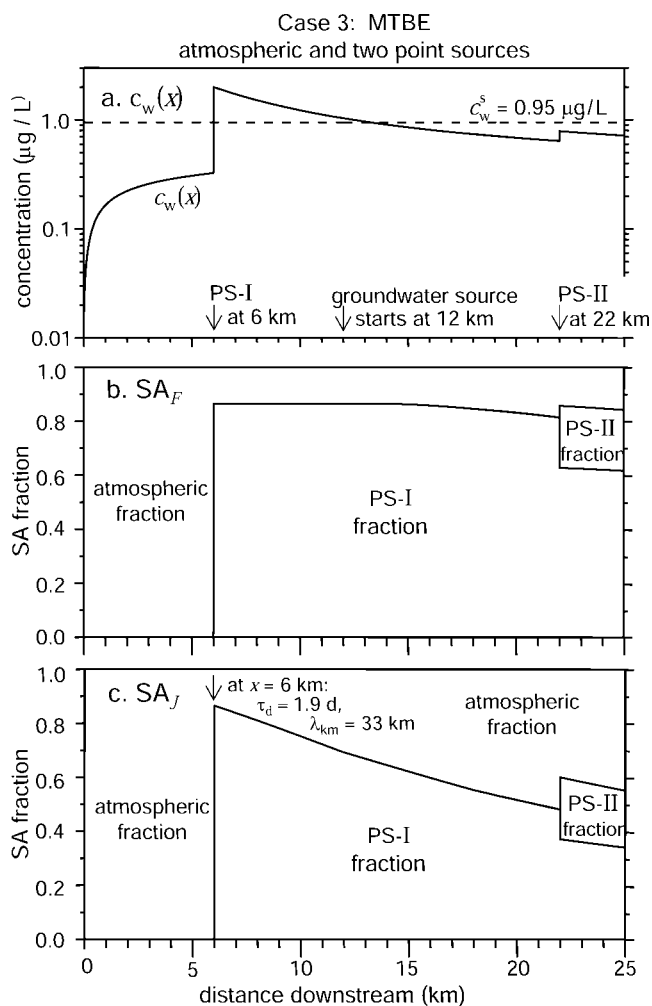


Fig. 7. (a) Stream concentration  $c_w(x)$ , (b) source apportionment ( $SA_F$ ), (c) source apportionment  $SA_J$  versus distance for methyl-*tert*-butyl ether (MTBE) in case 3. The MTBE in the atmosphere at  $0.026 \mu\text{g/L}$ , and in two point source (PS) effluent flows: PS-I,  $0.1 \text{ m}^3/\text{s}$  with MTBE at  $10.0 \mu\text{g/L}$ ; PS-II,  $0.1 \text{ m}^3/\text{s}$  with MTBE at  $3.3 \mu\text{g/L}$ . Ambient temperature =  $25^\circ\text{C}$ . Other conditions as given in Figure 4 and Appendix 3.

km, the inflow of groundwater containing chloroform at  $0.5 \mu\text{g/L}$  has two effects: the stream rapidly becomes supersaturated with chloroform relative to the concentration that would be specified by equilibrium with the atmosphere ( $c_w^s = 0.011 \mu\text{g/L}$ ) and the  $SA_F$  values (Fig. 6b) become different from the  $SA_J$  values (Fig. 6c). The supersaturation initiates chloroform outgassing to the atmosphere. The fact that the atmospheric-related  $SA_F$  fraction becomes ever smaller as  $x$  increases from 12 km toward 25 km is a consequence of continued addition of chloroform from groundwater for  $x > 12$  km and because the atmosphere-derived chloroform is outgassing (see Eqn. 11). For each  $x > 12$  km, the atmospheric-related fraction in the  $SA_J$  convention is higher than in the  $SA_F$  convention. This is a consequence of the continual introduction by  $J_{\text{abs}}$  of atmospherically assigned chloroform, even when  $F < 0$ .

#### Case 3 results—Atmospheric and point sources of MTBE and benzene

The case 3 results are presented in Figure 7 (MTBE) and Figure 8 (benzene).  $SA_F$  and  $SA_J$  results are equivalent for  $x < 6$  km, and observably different for  $x > 6$  km. Because there

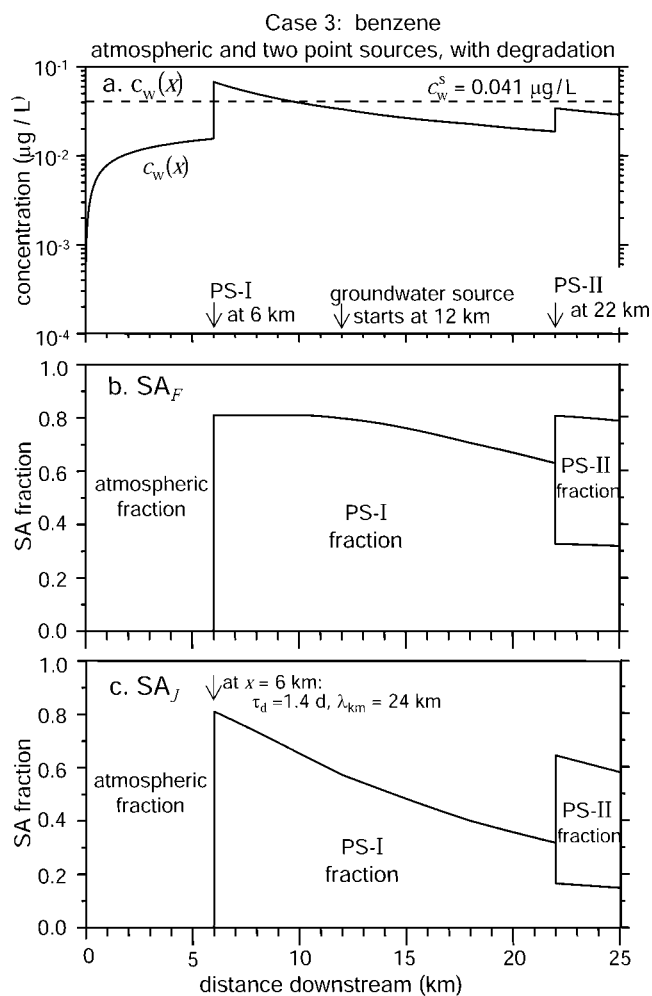


Fig. 8. (a) Stream concentration  $c_w(x)$ , (b) source apportionment ( $SA_F$ ), and (c) source apportionment  $SA_J$  versus distance for benzene in case 3. Benzene in the atmosphere at  $0.009 \mu\text{g/L}$  and in two point source (PS) effluent flows: PS-I,  $0.1 \text{ m}^3/\text{s}$  with benzene at  $1.0 \mu\text{g/L}$ ; PS-II,  $0.1 \text{ m}^3/\text{s}$  with benzene at  $0.3 \mu\text{g/L}$ . Ambient temperature =  $25^\circ\text{C}$ . Other conditions as given in Figure 4 and Appendix 3.

are no other sources of either MTBE or benzene over the first 6 km of the stream, the atmosphere accounts for 100% of each  $c_w(x)$  value from  $x = 0$  km up to 6 km in both the  $SA_F$  and  $SA_J$  conventions. As in cases 1 and 2, the stream does not approach equilibrium with the atmosphere, but by  $x \approx 5$  km does begin to approach steady concentrations of both MTBE and benzene ( $\sim 0.3 \mu\text{g/L}$ , and  $\sim 0.015 \mu\text{g/L}$ , respectively).

The composition and strength of PS-I was selected so that, at  $x = 6$  km, the stream concentrations of MTBE and benzene each rise instantaneously to about  $2c_w^s$ : the stream begins to outgas both MTBE and benzene. Outgassing for  $x > 6$  km continues until volatilization, dilution by the entry of VOC-free groundwater, and degradation (benzene only) reduce the  $c_w(x)$  values of MTBE and benzene so that they eventually become equal to their respective  $c_w^s$  values. At this point ( $x \approx 13$  and  $10$  km, for the two compounds, respectively), the atmospheric flux  $F = 0$ . Renewed input from the atmosphere begins as soon as  $c_w(x) < c_w^s$ . The more rapid decline in  $c_w(x)$  for benzene largely is due to the assumed degradation rate. (The gas/liquid transfer velocities of the two compounds are sufficiently similar for the model domain that differences in  $k_{OL}$  do not play a significant role in this comparison.) The



introduction of contaminant mass by PS-I causes differences between the  $SA_F$  and  $SA_J$  values for  $x > 6$  km.

We first consider the apportionment by the  $SA_F$  convention (Fig. 7b and Fig. 8b). As long as the initial outgassing ( $F < 0$ ) stage continues (MTBE,  $x = 6$  to  $\sim 13$  km; benzene,  $x = 6$  to  $\sim 10$  km), there is no change in the fractional  $SA_F$  distribution of either compound: the mass losses by volatilization (both compounds) and degradation (benzene only) are distributed proportionally over the fractions derived from the atmosphere and from PS-I ( $\alpha_{\text{atm}}$  and  $\alpha_{\text{PS-I}}$ , respectively). At  $x = 22$  km, the action of PS-II brings a third source into the SA mix and so both  $\alpha_{\text{atm}}$  and  $\alpha_{\text{PS-I}}$  drop at this point. However, PS-II does not cause  $c_w(x) > c_w^s$ ; so, for both compounds,  $\alpha_{\text{atm}}$  begins to grow again for  $x > 22$  km.

In the  $SA_J$  convention, as soon as compound mass is introduced by PS-I at  $x = 6$  km, the flux  $J_{\text{abs}}$  immediately begins to dilute that mass amount even though  $F < 0$ : The  $\alpha_{\text{atm}}$  for both compounds begins to grow at the expense of  $\alpha_{\text{PS-I}}$ . The fact that  $J_{\text{abs}}$  is capable of causing observable effects on  $\alpha_{\text{atm}}$  when  $F < 0$  (MTBE,  $6 \text{ km} < x < 13 \text{ km}$ ; benzene,  $6 \text{ km} < x < 10 \text{ km}$ ) is a consequence of the fact that  $\tau_d$  and  $\lambda_{\text{km}}$  take on values that are of similar scales as those that characterize the stream interval of interest. Indeed, at  $x = 6$  km, we have: stream depth  $h = 1$  m; stream velocity  $u = 0.2$  m/s;  $c_w/c_w^s = 2$  (MTBE) and  $c_w/c_w^s = 1.7$  (benzene); and  $k_{\text{OL}} = 1.2 \times 10^{-5}$  m/s (MTBE) and  $k_{\text{OL}} = 1.4 \times 10^{-5}$  m/s (benzene). These values give  $\tau_d = 1.9$  d and  $\lambda_{\text{km}} = 33$  km (MTBE), and  $\tau_d = 1.4$  d and  $\lambda_{\text{km}} = 24$  km (benzene).

#### Case 4a results—Atmospheric and other sources of PCE

The results for case 4a are presented in Figure 9. The  $SA_F$  and  $SA_J$  results are equivalent for  $x < 6$  km and different (but not observably different) for  $x > 6$  km. Because the atmosphere is the only source of PCE over the first 6 km of the stream, it accounts for 100% of each  $c_w(x)$  value as  $c_w(x)$  increases over that interval. As in cases 1 to 3, the stream does not approach equilibrium with the atmosphere; as  $x$  approaches 5 km, the PCE concentration does approach a relatively steady value of approximately  $0.002 \mu\text{g/L}$ . At  $x = 6$  km, PS-I causes the stream to become greatly supersaturated with PCE relative to the concentration that equilibrium with the atmosphere would specify ( $0.0056 \mu\text{g/L}$ ). The instantaneous, three-orders-of-magnitude rise in the PCE concentration in the stream thus obliterates the importance of the atmospheric fraction of the SA (though  $\alpha_{\text{atm}}$  is not reduced to zero) and begins strong outgassing of the PCE.

Due to the outgassing that continues for all  $x > 6$  km, the fractional distributions in the  $SA_F$  convention (see Fig. 9b) remain constant within each of the following intervals:  $6 \text{ km} \leq x < 12 \text{ km}$ ,  $15 \text{ km} \leq x < 22 \text{ km}$ , and  $x \geq 22 \text{ km}$ . At  $x = 25$  km, three of the four sources contribute significantly to the  $c_w(x)$  value of approximately  $2 \mu\text{g/L}$ ; these are PS-I, the non-point groundwater source, and PS-II. At  $x = 25$  km, the  $SA_F$  fractions for the three are 0.54, 0.35, and 0.11, respectively.

No significant differences can be observed when the  $SA_F$  results in Figure 9b are compared with the  $SA_J$  results in Figure 9c. This is a consequence of the enormous supersaturation ( $c_w/c_w^s \approx 1,000$ ) that characterizes the stream for all  $x \geq 6$  km. Indeed, at  $x = 6$  km,  $c_w/c_w^s$  rises to approximately 1,500. Taking  $h = 1$  m and  $k_{\text{OL}} \approx 1.4 \times 10^{-5}$  m/s, by Equation 21 for the region immediately downstream of  $x = 6$  km, we obtain  $\tau_d \approx 1,300$  d; as noted in Figure 4, the assumed stream conditions give a transit time of only 47 h ( $\approx 2$  d) for the assumed stream

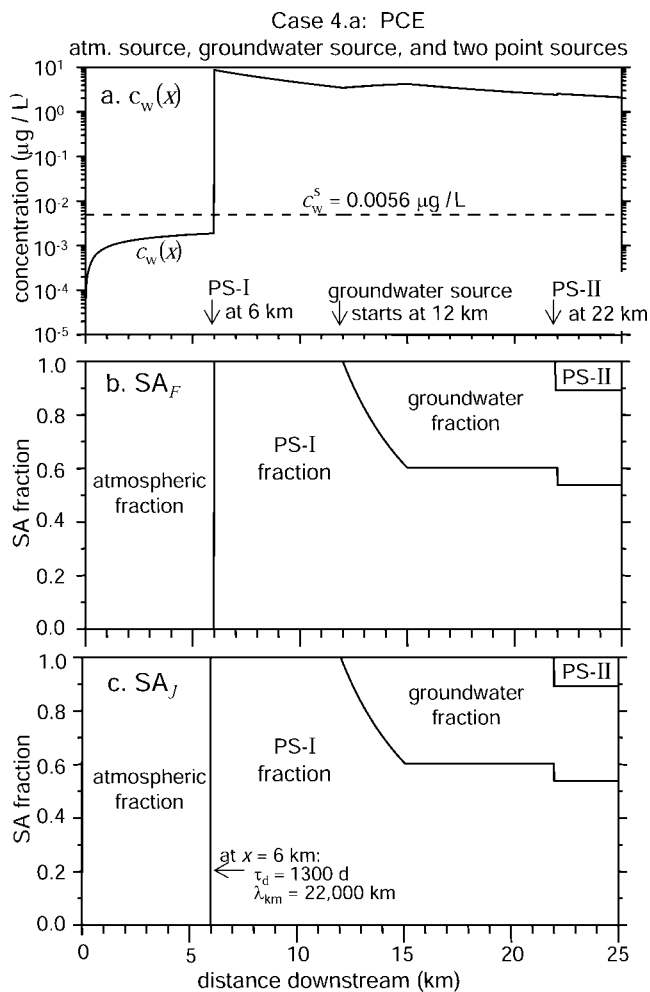


Fig. 9. (a) Stream concentration  $c_w(x)$ , (b) source apportionment  $SA_F$ , and (c) source apportionment ( $SA_J$ ) versus distance for perchloroethylene (PCE) in case 4a. The PCE in the atmosphere at  $0.0035 \mu\text{g/L}$  and in two point source (PS) effluent flows: PS-I,  $0.1 \text{ m}^3/\text{s}$  with PCE at  $50 \mu\text{g/L}$ ; PS-II,  $0.1 \text{ m}^3/\text{s}$  with PCE at  $5 \mu\text{g/L}$ . Also, PCE at  $10 \mu\text{g/L}$  in the groundwater flowing into the stream from  $x = 12$  to  $15$  km. Ambient temperature =  $25^\circ\text{C}$ . Other conditions as given in Figure 4 and Appendix 3.

length of 25 km. For a stream velocity of approximately  $0.2$  m/s by Equation 23,  $\tau_d \approx 1,300$  d corresponds to an enormous travel distance ( $\lambda_{\text{km}} \approx 22,000$  km). Thus it is clear why there are no observable differences between the  $\alpha$  values for  $SA_F$  and  $SA_J$  conventions in this case.

#### Case 4b results—Identical to case 4a but with point source I (PS-I) reduced 90%

Regulators and managers concerned with the quality of surface waters often seek to identify strategies for reducing contamination levels in streams. The SA model results such as those described above can provide valuable guidance in this regard. For the case 4a system, an example of such a strategy might be a  $10\times$  reduction for one of the sources. At  $x = 25$  km, the case 4a results indicate that PS-I is the most important source with  $\alpha_{\text{PS-I}} \approx 0.54$ . Thus one can predict that a 100% elimination PS-I would reduce  $c_w$  at  $x = 25$  km by approximately 54%, from approximately  $2 \mu\text{g/L}$  to  $0.92 \mu\text{g/L}$ . Reducing PS-I by 90% would produce nearly the same result, with  $c_w$  at  $x = 25$  km being lowered by approximately  $(0.90)(54\%) \approx 49\%$ . Case 4b thus considers the effect of re-

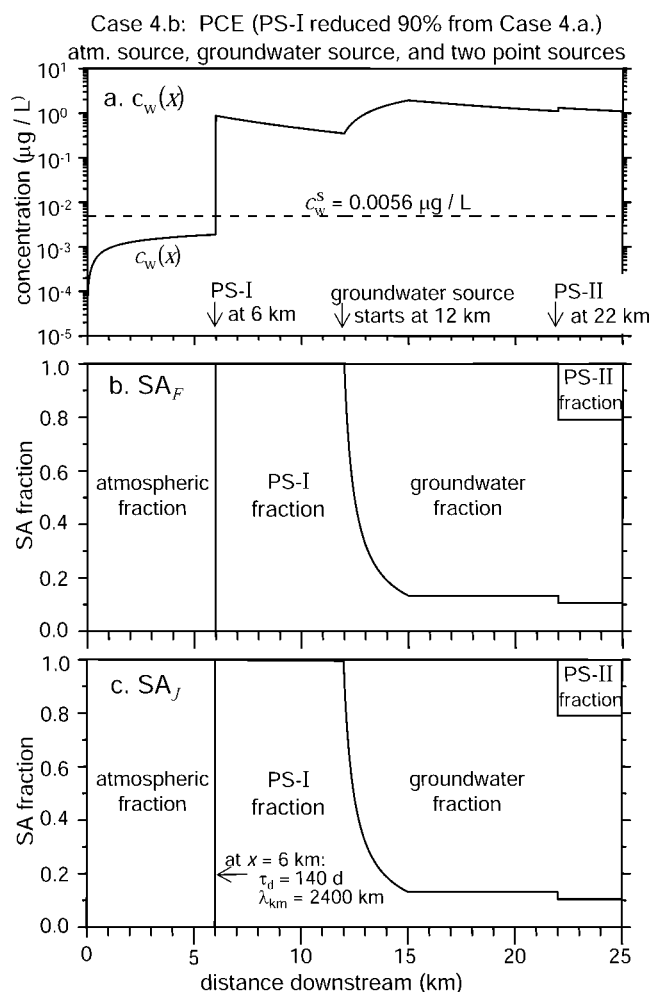


Fig. 10. (a) Stream concentration  $c_w(x)$ , (b) source apportionment ( $SA_F$ ), and (c) source apportionment  $SA_J$  versus distance for perchloroethylene (PCE) in case 4b. The PCE in the atmosphere at 0.0035  $\mu\text{g/L}$  and in two point source (PS) effluent flows: PS-I, 0.1  $\text{m}^3/\text{s}$  with PCE at 5  $\mu\text{g/L}$ ; PS-II, 0.1  $\text{m}^3/\text{s}$  with PCE at 10  $\mu\text{g/L}$  in the groundwater flowing into the stream from  $x = 12$  to 15 km. Ambient temperature = 25°C. Other conditions as given in Figure 4 and Appendix 3.

ducing the strength of PS-I by 90%; the results are presented in Figure 10. The new  $SA$  fractions at  $x = 25$  km are 0.10, 0.69, and 0.21 for PS-I, the nonpoint groundwater source, and PS-II, respectively. These  $SA$  fractions indicate that little would be achieved by further reduction of PS-I and that reduction of the nonpoint groundwater source next offers the greatest promise for reducing  $c_w$  at  $x = 25$  km. Lastly, we note that reducing PS-I by 90% reduces  $\tau_d$  at  $x = 6$  km from approximately 1,300 d to approximately 140 d, and  $\lambda_{\text{km}}$  from 22,000 km to 2,400 km. However, the reduced values still are far too large to allow any observable differences between the  $SA_F$  and  $SA_J$  plots in Figure 10.

### CONCLUSION

Interest is likely to increase in  $SA$  modeling of VOCs in streams, especially in light of recent findings that VOCs frequently are found in the source water of many community water systems [33,34]. Most water contamination found at the 1- to 10- $\mu\text{g/L}$  level and higher probably is due to some type of land-based source, though an urban atmosphere can lead to

$c_w$  values of a few compounds (e.g., acetone and MTBE) at levels up to approximately 10- $\mu\text{g/L}$ .

Two  $SA$  rules allow  $SA$  modeling of volatilizable compounds in streams in a manner that permits the tracking of the relative importance of all possible point and nonpoint sources, including the atmosphere. The different cases considered here illustrate that any number of different cases can be modeled. Application of the  $SA$  rules according to the two different conventions for handling input from the atmosphere can lead to either very different or very similar  $SA$  allocations. Differences tend to be observed between results obtained by the  $SA_F$  and  $SA_J$  conventions when a nonatmospheric source of contamination leads to a small value of  $c_w/c_w^s$  (e.g., 1 or less), and when the stream is shallow (small  $h$ ), fast-moving (high  $k_{OL}$ ), and long enough for  $J_{\text{abs}}$  to affect the makeup of  $c_w$ . Source apportionment modeling provides the framework necessary for comparing different strategies for mitigating contamination at points of interest along a stream.

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#### APPENDIX 1

Conditions, conclusions, and analytic solution for a simple hypothetical source apportionment (SA) case involving a stream flowing from a pristine region into an urban region that

is contaminated by compound X (see Fig. 3). The degradation loss rate of X in the water is assumed to be zero.

Concentration and net flux ( $F$ ) conditions for compound X

Pristine region	Urban region
$c_g = 0$	$c_g \neq 0$
$c_w = 0$	$c_w = c_g[H/(RT)]$
$F = 0$	$F = 0$

SA conclusions for compound X in urban region

SA <sub>F</sub> convention	SA <sub>J</sub> convention
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At point A:

$$\alpha_{\text{leak}} = 1$$

$$\alpha_{\text{atm}} = 0$$

At point A:

$$\alpha_{\text{leak}} = 1$$

$$\alpha_{\text{atm}} = 0$$

Downstream of A:

$$\alpha_{\text{leak}} = 1$$

$$\alpha_{\text{atm}} = 0$$

Downstream of A:

$$\alpha_{\text{leak}} \rightarrow 0$$

$$\alpha_{\text{atm}} \rightarrow 1$$

Analytic solution in urban region for stream that is uniform with distance (constant discharge  $Q$ , width  $w$ , and depth  $h$ ) for SA<sub>J</sub> convention:

$$\alpha_{\text{atm}}(t) = 1 - \exp[-(k_{\text{OL}}/h)t]$$

$$\alpha_{\text{leak}}(t) = 1 - \alpha_{\text{atm}}(t)$$

$$= \exp[-(k_{\text{OL}}/h)t]$$

where  $k_{\text{OL}}$  (m/s) = overall mass transfer coefficient,  $h$  (m) = average stream depth, and  $t$  (s) = time with  $t = 0$  at point A.

#### APPENDIX 2

General and convention-specific elements of source apportionment (SA) modeling for a volatilizable compound

1. General. The mass input from each source  $j$  is labeled and counted towards the  $c_j$  portion of  $c$  with

$$c_w = \sum_j c_{w,j} = c_{w,1} + c_{w,2} + c_{w,3} + \dots$$

- 2.a. Atmospheric stream fluxes—SA<sub>F</sub> convention. The net flux  $F$  between the atmosphere and the stream surface is a first-order kinetic process:

$$F (\mu\text{g}/\text{m}^2 - \text{s}) = 10^3 k_{\text{OL}}(c_w^s - c_w)$$

- 2.a.1. When  $F > 0$ , all input mass is assigned to the  $j = \text{atm}$  (atmospheric) portion of  $c_w$  (application of SA rule 1).

- 2.a.2. When  $F < 0$ , the losses from  $c_w$  are distributed over all of the  $c_{w,j}$  values according to the  $\alpha_j$  values (application of SA rule 2).

- 2.b. Atmospheric stream fluxes—SA<sub>J</sub> convention. The absorptive flux  $J_{\text{abs}}$  from the atmosphere ( $j = \text{atm}$ ) into the stream is given by

$$J_{\text{abs}} (\mu\text{g}/\text{m}^2 - \text{s}) = 10^3 k_{\text{OL}}c_w^s (>0)$$

The simultaneous volatilization flux  $J_{\text{vol}}$  from the stream to the atmosphere is given by

$$J_{\text{vol}} (\mu\text{g}/\text{m}^2 - \text{s}) = 10^3 k_{\text{OL}}c_w (>0)$$

- a. All mass input by  $J_{\text{abs}}$  is assigned to the  $j = \text{atm}$  (atmospheric) portion of  $c_w$  (application of SA rule 1).
- b. Mass lost by  $J_{\text{vol}}$  is distributed over all of the  $c_{w,j}$  values according to the  $\alpha_j$  values (application of SA rule 2).

3. Degradation. The losses from  $c_w$  are distributed over all  $j$  components of  $c_w$  according to the  $\alpha_j$  values.
4. Stream-groundwater interactions.
  - a. Groundwater inflow to stream. One hundred percent of the input from each distinct groundwater source is assigned to a separate  $c_{w,j}$ . (For hyporheic inflow, it is necessary to have tracked the components of the concentration within the associated groundwater flowpaths so that proper reallocations to the stream  $c_{w,j}$  values can be made as the flowpaths emerge from the stream bottom.)
  - b. Stream loss to groundwater. The mass loss of the compound from the stream is distributed over the  $j$  components according to the  $\alpha_j$  values.

### APPENDIX 3

Model parameters for four example cases for source apportionment (SA) modeling of volatile organic compounds (VOCs) in a stream (see also Fig. 4).

1. Stream and environmental parameters (assumed).
  - a. 25-km-long stream section
  - b. Linear increase in stream flow from 0.05 to 2.05 m<sup>3</sup>/s due to perennial groundwater flow;
  - c. Stream depth: 0.5 m (from  $x = 0$  to 6 km), then 1.0 m (from  $x = 6$  to 12 km), then 1.5 m (from  $x = 12$  to 18 km), then 2.0 m (from  $x = 18$  to 25 km)
  - d. Stream width: 2.0 m (from  $x = 0$  to 6 km), then 3.0 m (from  $x = 6$  to 12 km), then 4.0 m (from  $x = 12$  to 18 km), then 5.0 m (from  $x = 18$  to 25 km)
  - e. Stream velocity  $u$ : 0.04 to 0.205 m/s
  - f. Constant temperatures: water = 25°C, air = 25°C ( $T = 298$  K)
  - g. Constant wind speed: 4.0 m/s;
  - h. Air/water partitioning parameters and U.S. Environmental Protection Agency (U.S. EPA) maximum contaminant level (MCL) values for methyl-*t*-butyl ether (MTBE), acetone, chloroform, and perchloroethene (PCE):

	$H/RT$ (25°C)	$c_g$ (µg/L)	$c_w^s$ (µg/L)	U.S. EPA MCL <sup>a</sup> (µg/L)
MTBE	0.027	0.026	0.95	NR <sup>b</sup>
Acetone	0.0021	0.14	67.00	NR
Chloroform	0.17	0.0019	0.011	NR
Benzene	0.22	0.0090	0.041	5
PCE	0.62	0.0035	0.0056	5

<sup>a</sup> MCL = maximum containment level.

<sup>b</sup> NR = no regulation.

- i. Gas/liquid transfer velocity  $k_{OL}$  at 25°C (m/s) calculated for the stream based on flow conditions following Rathbun [23] based on

$$1/k_{OL} = 1/k_L + 1/[(H/RT)k_G]$$

where  $k_L$  is the liquid-side mass-transfer velocity that depends on stream velocity, stream depth, and the diffusivity of the compound in water [35] and  $k_G$  is the air-side mass-transfer velocity that depends on wind speed and the diffusivity of the compound in air

Log  $k_{OL}$  (m/s) for range of conditions in the model stream (see Fig. 4)

MTBE:	-5.72 to -4.62
Benzene:	-5.68 to -4.54
Acetone:	-5.70 to -4.96
PCE:	-5.66 to -4.49
Chloroform:	-5.66 to -4.51

- j. Biodegradation rate constant for benzene  $k_{deg} = 0.43$  d<sup>-1</sup>
2. Source parameters for cases 1, 2, 3, 4.a, and 4.b.

Levels and source characteristics

Case	Compounds	Point source			Groundwater nonpoint source (12-25 km for case 3; 12-15 km for case 4)
		Atmosphere (air)	I (PS-I) 0.10 m <sup>3</sup> /s at $x = 6$ km	II (PS-II) 0.10 m <sup>3</sup> /s at $x = 6$ km	
1	MTBE	0.026 µg/L	0	0	0
	Acetone	0.140 µg/L	0	0	0
2	Chloroform	0.0019 µg/L	0	0	0.5 µg/L
3	MTBE	0.026 µg/L	10.0 µg/L	3.3 µg/L	0
	Benzene	0.009 µg/L	1.0 µg/L	0.3 µg/L	0
4.a	PCE	0.0035 µg/L	50.0 µg/L	5.0 µg/L	10.0 µg/L
4.b	PCE	0.0035 µg/L	5.0 µg/L	5.0 µg/L	10.0 µg/L