

**NATIONAL WATER-QUALITY ASSESSMENT PROGRAM  
NATIONAL SYNTHESIS ON VOLATILE ORGANIC COMPOUNDS**

# **StreamVOC—A Deterministic Source- Apportionment Model to Estimate Volatile Organic Compound Concentrations in Rivers and Streams**

Scientific Investigations Report 2006–5110



# **StreamVOC—A Deterministic Source- Apportionment Model to Estimate Volatile Organic Compound Concentrations in Rivers and Streams**

By William Asher, David A. Bender, John S. Zogorski, and Roy C. Bartholomay

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## Symbols, Derivatives, Units of Measurement, and Abbreviations

Symbol	Description	Unit of measurement
$A_i$	compound-dependent constant in $T_w$ -dependent equation for $H_i$	
$a$	exposed stream surface seen by flow $Q$ (note: $a = Q/h$ )	$m^2/s$
$B_i$	compound-dependent constant in $T_w$ -dependent equation for $H_i$	
$c_{d,i}$	concentration of contaminant $i$ in stream immediately downstream from a hydraulic structure	$mol/m^3$
$c_{gw,i}$	concentration of contaminant $i$ in ground water entering the stream	$mol/m^3$
$c_i$	overall concentration of contaminant $i$ at point $(x,y,z,t)$	$mol/m^3$
$\Delta c_i$	concentration difference used to express the air-water mass transfer rate	$mol/m^3$
$c_{i,j}$	portion of the concentration of $c_i$ that is due to source $j$	$mol/m^3$
$c_0$	concentration of contaminant $i$ at the upstream end of the modeled region	$mol/m^3$
$c_{i,k}^{mod}$	surface-water concentration of contaminant $i$ in zone $k$ calculated by StreamVOC	$mol/m^3$
$c_{i,k}^{ss}$	surface-water concentration of contaminant $i$ in zone $k$ measured during the synoptic study	$mol/m^3$
$c_{s,i}$	water concentration of $i$ that would be in "saturation" equilibrium at $T_w$	$mol/m^3$
$c_{u,i}$	concentration of contaminant $i$ in stream immediately upstream from a hydraulic structure	$mol/m^3$
$D_i$	diffusivity of contaminant $i$ in water at $T_w$	
$D_{O_2}$	diffusivity of oxygen in water at 293.16 K	
$d$	depth of flow through hyporheic zone under a hydraulic structure	m
$E_{20}$	transfer efficiency for oxygen at 293.16 K at a hydraulic structure	
$E_i$	transfer efficiency of a contaminant with diffusivity equal to $D_i$ at $T_w$ but the solubility of oxygen at 293.16 K	
$E_i(H_i)$	transfer efficiency of a contaminant with diffusivity equal to $D_i$ at $T_w$ and solubility equal to $H_i$ at $T_w$	
<b>F</b>	Froude number of flow over a hydraulic structure	
$F_{air,i}$	the net air-water flux of VOC $i$	$mol/(m^2 \cdot s)$
$F_{over}$	fraction of total streamflow that flows over a dam or weir	
$F_{under}$	fraction of total streamflow that flows under dam or weir in hyporheic region	
$f$	compound and temperature specific correction factor for $E_{20}$	
$f_i$	local fraction for $i$ of the total ambient atmospheric pressure	ppbv
$g$	acceleration of gravity	$m^2/s$
$H$	hydraulic head	m
$H_i$	compound- and temperature-dependent Henry's Gas Law constant for $i$	$m^3 \cdot atm/mol$
$h$	average stream depth at point $(x, y = 0, t)$	m
$h_T$	depth of tailwater downstream from weir	m
$i$	index for the contaminant of interest	
$i,j$	fractional change in concentration of $i$ in source $j$	

Symbol	Description	Unit of measurement
$J_{\text{abs},i}$	the flux of VOC $i$ from the atmosphere into the water	mol/(m <sup>2</sup> -s)
$J_{\text{vol},i}$	the flux of VOC $i$ from the water into the atmosphere	mol/(m <sup>2</sup> -s)
$j$	index for the source of interest (note: maximum value of $j$ is $N_s$ )	
$k$	index for the point source of interest (note: maximum value of $k$ is $N_{\text{ps}}$ )	
$k_{\text{deg},i}$	first-order degradation rate constant for $i$	1/s
$k_{\text{G},i}$	local mass transfer velocity for $i$ through the air-side layer	m/s
$k_{\text{L},i}$	local mass transfer velocity for $i$ through the water-side layer	m/s
$k_{\text{OA},i}$	local overall gas exchange velocity for VOC $i$	m/s
$k_{\text{OL},i}$	local overall air-water mass transfer velocity for $i$	m/s
$k_2^{20}$	rate constant for air-water mass transfer (“reaeration”) of oxygen at 20°C ( $T_w = 293.15$ K)	1/day
$k^\theta$	rate constant for air-water mass transfer of oxygen at $\theta^\circ\text{C}$ ( $T_w = \theta + 293.15$ K)	1/day
$L^2$	total length of stream	km
$M_{i,j}$	mass of VOC $i$ due to source $j$ per unit volume of stream water	mol/s
$M_i$	mass of VOC $i$ per unit volume of stream water	mol/s
$MW_i$	molecular weight of $i$	g/mol
$m_{\text{in},i}$	differential input rate for $i$ from all local sources (including ground-water inflow)	mol/m-s
$N$	number of significant digits required in the model output	
$N_{\text{C},i}$	number of non-zero surface-water concentration measurements for $i$	
$N_{\text{ps}}$	number of point sources in system	
$N_s$	total number of sources in the system	
$P$	local total ambient atmospheric pressure	atm
$p_i$	local gas-phase pressure of $i$ in the ambient air	atm
$Q$	streamflow at point $(x, t)$	m <sup>3</sup> /s; ft <sup>3</sup> /min
$Q_{\text{under}}$	streamflow under a hydraulic structure through the hyporheic zone	m <sup>3</sup> /s
$\Delta Q$	change in streamflow	ft <sup>3</sup> /min
$q$	specific flow over a hydraulic structure (= $Q$ divided by structure width)	m <sup>2</sup> /s
$R$	universal gas constant	m <sup>3</sup> -atm/K-mol
$\mathbf{R}$	Reynolds number of flow over hydraulic structure	
$r$	gas concentration deficit over a hydraulic structure	
$r_{\text{Hi}}$	gas concentration deficit for contaminant $i$	
$S$	cross-sectional area for flow through hyporheic zone under a hydraulic structure	m <sup>2</sup>
$s$	submergence depth of sill lip for gated spillway	m
$T_A$	air temperature	°C
$T_w$	local bulk water temperature in the stream	K; °C
$t$	time	s
$t_k$	time the $k$ 'th point source enters the stream	s
$U$	wind speed	m/s
$u$	linear flow velocity in stream	m/s

Symbol	Description	Unit of measurement
$\bar{u}_{sz}$	average stream velocity over a subzone	m/s
$\Delta[\text{VOC}]_i$	difference between the modified source concentration and the source concentration determined from the synoptic study data set	
$[\text{VOC}]_{i,\text{AVG}}$	average concentration of the VOC over the synoptic study zone.	
$\bar{V}_i$	molar volume of $i$	$\text{cm}^3/\text{mol}$
$w$	average stream width at point $(x, t)$	m
$x$	longitudinal distance (Eulerian) along a stream ( $x = 0$ at the <i>upstream</i> end of the modeled stream section)	m
$\Delta x_{\text{ps}}$	length of stream over which point source is active	m
$\Delta x_{\text{sz}}$	length of the subzone	m
$y$	horizontal transverse distance (Eulerian) in stream ( $y = 0$ at stream center)	m
$z$	vertical transverse distance (Eulerian) in stream ( $z = 0$ at stream surface)	m
$\alpha_{i,j}$	fraction of the concentration of $c_i$ that is due to source $j$	
$\alpha_{\text{d},i,j}$	fraction of concentration of $c_i$ that is due to source $j$ contaminant immediately downstream from a hydraulic structure	$\text{mol}/\text{m}^3$
$\alpha_{\text{PS}}$	SA fraction from a point source	
$\alpha_{\text{NPS}}$	SA fraction from a nonpoint source	
$\alpha_{\text{u},i,j}$	fraction of concentration of $c_i$ that is due to source $j$ contaminant immediately upstream from a hydraulic structure	$\text{mol}/\text{m}^3$
$\alpha_{\text{d},i,\text{air}}$	SA fraction for atmospheric source downstream from the hydraulic structure	$\text{mol}/\text{m}^3$
$\alpha_{\text{u},i,\text{air}}$	upstream SA fraction for the atmospheric source term $i$	$\text{mol}/\text{m}^3$
$\beta_i$	normalized fractional change of the concentration of $\text{VOC}_i$ in source $j$	
$\gamma_{i,j}$	normalized difference between measured and modeled concentrations	
$\delta$	Kronecker delta function	
$\eta$	head loss across hydraulic structure	m
$\theta$	bulk stream-water temperature (note: $\theta = T_w - 273.15$ )	$^{\circ}\text{C}$
$\kappa$	hydraulic conductivity	m/s
$\nu$	kinematic viscosity of water	$\text{m}^2/\text{s}$
$\phi_{\text{gw}}(t)$	rate at which ground water enters or leaves the stream water as a function of time	$\text{m}^3/\text{s}^2$
$\phi_{\text{ps}}$	flow of water entering stream from a point source	$\text{m}^3/\text{s}$
$\Phi_{\text{gw}}$	rate at which streamflow discharge is lost by water outflow to ground water or a point withdrawal	$\text{m}^3/\text{s}^2$
$\Phi_{\text{gw},c_i}$	differential rate at which discharge of $i$ is reduced due to water outflow to ground water	$\text{mol}/\text{s}^2$
$\Phi_{\text{out}}$	differential rate at which stream-water discharge is lost by water outflow to ground water or to a point withdrawal	$\text{m}^3/\text{s}^2$
$\rho_{i,j}$	fractional change in concentration of $i$ in source $j$	
$\tau_{0.5,i}$	degradation half-life of $i$	
$\chi_i^2$	reduced chi-square optimization parameter	m/s

<b>Derivatives</b>		
$dc_i/dt$	time rate of change of concentration of $i$ at point $(x,t)$	$\text{mol/m}^3\text{-s}$
$d\alpha_{i,j}/dt$	time rate of change in source apportionment of source $j$ for $\text{VOC}_i$	
$dM_{i,j}/dt$	change in mass of $\text{VOC } i$ due to source $j$ in the time interval defined by $dt$	$\text{mol/s}^2$
$dM_i/dt$	total change in mass of $\text{VOC } i$ in the time interval defined by $dt$	$\text{mol/s}^2$
$dQ/dt$	change in streamflow volume in the time interval defined by $dt$	$\text{m}^3/\text{s}^2$
<b>Units of measurement</b>		
atm	atmosphere	
$\text{cm}^3/\text{mol}$	cubic centimeters per mole	
ft	feet	
$^{\circ}\text{C}$	degrees Celsius	
$\text{ft}^3/\text{min-km}$	cubic foot per minute per kilometer	
g/mol	grams per mole	
K	degrees Kelvin	
km	kilometer	
m	meter	
m/s	meters per second	
$\text{m}^2/\text{s}$	meters squared per second	
$\text{m}^3/\text{s}$	cubic meters per second	
$\text{m}^3\text{-atm/K-mol}$	cubic meters atmosphere per Kelvin per mole	
$\text{m}^3/\text{s-km}$	cubic meters per second per kilometer	
$\text{m}^3/\text{s}^2$	cubic meters per square second	
$\text{m}^3\text{-atm/mol}$	cubic meters atmosphere per mole	
mol	moles	
$\text{mol/m-s}$	moles per meter per second	
$\text{mol/s}^2$	moles per square second	
$\text{mol/m}^3$	moles per cubic meter	
$\text{mol/m}^3\text{-s}$	moles per cubic meter per second	
ppbv	parts per billion by volume	
s	second	
$\mu\text{g/L}$	micrograms per liter	
$\mu\text{g/L-s}$	micrograms per liter per second	
<b>Abbreviations</b>		
ACE	acetone	
BEN	benzene	
CLF	chloroform	
1-D	one-dimensional	
1,1-DCA	1,1-dichloroethane	
<i>cis</i> -1,2-DCE	<i>cis</i> -1,2-dichloroethene	
DEQ	differential equation	
EDT	Eastern Daylight Time	
GPS	global positioning system	
MDL	method detection limit	

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**Abbreviations—Continued**

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MTBE	methyl <i>tert</i> -butyl ether
NAWQA	National Water-Quality Assessment Program of the U.S. Geological Survey
ND	not detected
NPS	nonpoint source
PS	point source
PCE	perchloroethene (also known as tetrachloroethene)
SA	source apportionment
TCE	trichloroethene
VOC	volatile organic compound
<	less than
>	greater than

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# StreamVOC—A Deterministic Source-Apportionment Model to Estimate Volatile Organic Compound Concentrations in Rivers and Streams

By William E. Asher, David A. Bender, John S. Zogorski, and Roy C. Bartholomay

## Abstract

This report documents the construction and verification of the model, StreamVOC, that estimates (1) the time- and position-dependent concentrations of volatile organic compounds (VOCs) in rivers and streams as well as (2) the source apportionment (SA) of those concentrations. The model considers how different types of sources and loss processes can act together to yield a given observed VOC concentration. Reasons for interest in the relative and absolute contributions of different sources to contaminant concentrations include the need to apportion: (1) the origins for an observed contamination, and (2) the associated human and ecosystem risks. For VOCs, sources of interest include the atmosphere (by absorption), as well as point and nonpoint inflows of VOC-containing water. Loss processes of interest include volatilization to the atmosphere, degradation, and outflows of VOC-containing water from the stream to local ground water.

This report presents the details of StreamVOC and compares model output with measured concentrations for eight VOCs found in the Aberjona River at Winchester, Massachusetts. Input data for the model were obtained during a synoptic study of the stream system conducted July 11–13, 2001, as part of the National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey. The input data included a variety of basic stream characteristics (for example, flows, temperature, and VOC concentrations). The StreamVOC concentration results agreed moderately well with the measured concentration data for several VOCs and provided compound-dependent SA estimates as a function of longitudinal distance down the river. For many VOCs, the quality of the agreement between the model-simulated and measured concentrations could be improved by simple adjustments of the model input parameters. In general, this study illustrated: (1) the considerable difficulty of quantifying correctly the locations and magnitudes of ground-water-related sources of contamination in streams; and (2) that model-based estimates of stream VOC concentrations are likely to be most accurate when the major sources are point sources or tributaries where the spatial extent and magnitude of the sources are tightly constrained and easily determined.

## Introduction

The National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey seeks to understand the sources and processes that determine the concentrations, transport, and fate of contaminants in the natural waters of the United States (Gilliom and others, 1995). Contaminant groups of interest include volatile organic compounds (VOCs), pesticides, nutrients, trace elements, and major ions. For urban streams, NAWQA results indicate the frequent presence of multiple dissolved VOCs (Gilliom and others, 1995; Lopes and Price, 1997). An adequate understanding, however, does not exist for the identities and relative roles of the typical contaminant sources that lead to the observed VOC concentrations, nor for the coupled manners in which physical, chemical, and biological processes in streams act on those contributions to yield observed position- and time-dependent concentrations. There is interest in the continued development of “source apportionment” (SA) modeling principles for use in tracking 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 to VOC concentrations include the need to apportion: (1) the origins for observed contamination; and (2) the associated human and ecosystem risks.

Pankow and others (2006) provided a theoretical framework for SA modeling in streams. For each contaminant  $i$  and each stream point  $(x,y,z,t)$ , they define  $\alpha_{i,1}, \alpha_{i,2}, \dots, \alpha_{i,N_s}$  as the SA fractions due to the total number of different sources ( $N_s$ ) acting along a stream, which can be written as:

$$\alpha_{i,j} = \frac{c_{i,j}}{c_i} = \frac{M_{i,j}}{M_i}, \quad (1)$$

where  $c_{i,j}$  ( $\text{mol}/\text{m}^3$ ) is the portion of the concentration of  $c_i$  ( $\text{mol}/\text{m}^3$ ) that is due to source  $j$ . For each  $i$ ,  $\alpha_{i,1} + \alpha_{i,2} + \dots + \alpha_{i,N_s} = 1$ ,  $M_i$  ( $\text{mol}/\text{s}$ ) is the rate at which the stream discharges compound  $i$ , and  $M_{i,j}$  ( $\text{mol}/\text{s}$ ) is the  $j$ -related portion of that discharge.

When a contaminant  $i$  is subject to air/water partitioning according to Henry's Gas Law, as are the VOCs, then  $c_{s,i}$  is

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defined as the water concentration of  $i$  that would be present at equilibrium with the local air. Pankow and others (2006) described three possibilities: (1)  $c_i > c_{s,i}$  so that  $i$  is volatilizing from the stream to the atmosphere; (2)  $c_i < c_{s,i}$  so that  $i$  is being absorbed from the atmosphere into the stream; or (3)  $c_i = c_{s,i}$  so that  $i$  is neither volatilizing from the stream, nor being absorbed from the atmosphere. The direction and magnitude of the flux will thus depend on the local values of the concentrations in the adjacent air and water phases, and on  $H_i$  ( $\text{m}^3\text{-atm/mol}$ ), which is the compound- and temperature-dependent Henry's Gas Law equilibrium constant.

Pankow and others (2006) showed that the first two possibilities described previously ( $c_i > c_{s,i}$  and  $c_i < c_{s,i}$ ) lead directly to two SA rules governing calculation of  $\alpha$  values for VOCs:

1. wherever and whenever a stream is absorbing  $i$  from the atmosphere, the air-to-water flux causes a corresponding increase in the particular  $c_{i,j}$  that is related to the atmosphere; and
2. wherever and whenever volatilization loss occurs from the stream, the water-to-air loss acts to diminish all of the local  $c_{i,j}$  (including the particular, atmospheric  $c_{i,j}$ ) by degrees that are in proportion to their corresponding local  $\alpha_{i,j}$  values.

Pankow and others (2006) explained that the second rule extends to losses by mechanisms other than volatilization (for example, it extends to losses of  $i$  from the stream due to biological and abiotic degradation, water removal by infiltration to ground water, and others). As a result, at any point  $(x,y,z,t)$ , the set of  $\alpha_{i,j}$  values for a given contaminant  $i$  will not change whenever contaminant mass is lost from a stream; changes in a set of  $\alpha_{i,j}$  only can occur when one or more sources act to add contaminant mass at  $(x,y,z,t)$  (Pankow and others, 2006).

A deterministic SA model, StreamVOC, was developed to estimate VOC concentrations in rivers and streams. The model considers how different types of sources and loss processes can act together to yield an observed VOC concentration.

### Purpose and Scope

The purpose of this report is to document StreamVOC, which is a source-apportionment model to estimate total VOC concentrations and the SA fractions as a function of distance in rivers and streams. User instructions and information needs for running StreamVOC are described. The numerical performance and behavior of the model is verified using input data constructed for a hypothetical stream and input data collected during a source-synoptic study of the Aberjona River in Winchester, Massachusetts. As basic input, StreamVOC requires the river depth and width as a function of position, river flow rates, inflows from tributaries, ground-water inflow and loss along the river, and VOC concentrations in tributaries and ground-water sources. For StreamVOC, the river is assumed to be well mixed vertically and accounts for VOC losses through biological/chemical degradation, ground-water recharge, and air-water gas exchange. User-entered model parameters include

wind speed, air and water temperature, atmospheric pressure, relative humidity, atmospheric VOC concentration, stream depth as a function of position, stream width as a function of position, VOC inputs to the stream other than the atmosphere, surface-water degradation rates, diffusivity parameters, solubility parameters, and the molecular weight of the VOC.

### Acknowledgments

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## Description and Theoretical Basis of StreamVOC

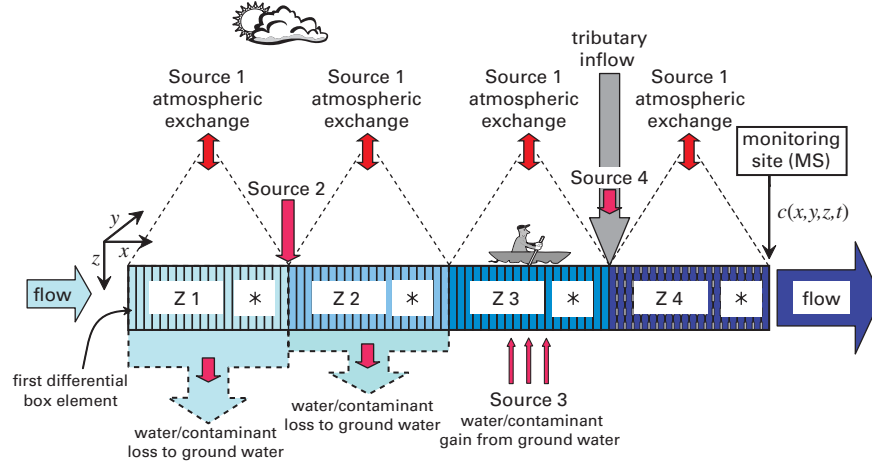
This section presents a general description, governing equations, and physicochemical parameterizations for StreamVOC. Model operation and numerical methods are described.

### General Description

The one-dimensional (1-D) version of StreamVOC described in this report assumes that a stream with total length  $L$  (km) can be divided into a finite number of separate, longitudinal zones. It is assumed that each zone can be characterized by a constant average stream depth  $h$  (m) and a constant average width  $w$  (m). Within a given zone, however, the total stream-flow  $Q$  ( $\text{m}^3/\text{s}$ ) and velocity  $u$  (m/s) may change due to stream-flow gains (or losses) from (to) ground water. The zone boundaries are defined as the particular distances  $x$  along the stream at which there is: (1) a change in  $h$  or  $w$ ; (2) a tributary inflow that may or may not contain contaminant(s) of interest; and/or (3) one or more point sources that add contaminant mass. Because of the third possibility, a set of model zones, in general, will not correspond to a set of stream "reaches" that would be defined by flow characteristics alone. Within a given zone, contaminant mass may enter a stream from a distributed source (as from the nonpoint inflow of contaminated ground water), a point source (such as from tributary inflow), or from the atmosphere. Contaminant mass may be lost within a zone by volatilization to the atmosphere, degradation, and/or outflow of stream water to local ground water.

Figure 1 shows a hypothetical stream with four zones each characterized by a depth ( $h_i$ ) and width ( $w_i$ ) and four VOC sources (the atmosphere, two point sources, and a distributed source related to ground-water inflow). There also are two areas of stream outflow to ground water. The stream data required to initialize the model presented are  $h_i$ ,  $w_i$ , and  $Q_i$  for each zone, the atmospheric VOC concentration, the VOC concentrations in





**Figure 1.** Schematic representation of a portion of an example stream that is characterized by a series of four distinct hydrologic zones (Z1–Z4). The zone boundaries correspond to changes in stream width or depth, or could reflect the presence of tributaries or point sources. Monitoring site (MS) is shown at which the concentration  $c(x,y,z,t)$  is of particular interest. For modeling purposes, each zone is discretized into a series of sequential box elements. Four sources (S1–S4) of a volatile organic compound (VOC) of interest are shown. The possibility of contaminant loss by degradation within *each* box element in each reach is represented with the symbol \*. The VOC will tend to exchange with the atmosphere from the surface area of each box element. On the ground-water side, water loss and associated VOC loss, or water gain and associated VOC gain, may be prescribed for each differential box element.

each point source and in ground-water inflow, the ground-water inflow and outflow volumes, and the flow volumes for the two point sources. Other ancillary data required include the air/water temperature, atmospheric pressure, average wind speed, and knowledge of the molecular diffusivity and solubility of the VOC.

Parameters are entered through an ASCII parameter file. Numerical output from the model is displayed graphically and saved to an optional ASCII data file.

## Governing Equations

StreamVOC tracks the SA of a VOC in a Lagrangian manner as a parcel of water moves downstream. At any given point in the stream, the volume of the parcel corresponds to 1 second's worth of flow, and therefore equals  $Q \times 1$  s. Consequently, the flow gains and losses experienced by the stream cause the parcel to undergo changes in volume as a function of  $t$ . Changes in  $c_i$  can thus be caused by contaminant addition or loss, as well as by changes in  $Q$ . (This approach simplifies consideration of the effects of dilution and mixing at confluences because flows at confluences are directly additive.) For VOC  $i$ , the time rate of change in a vertically and laterally mixed stream thus can be written as:

$$\frac{dc_i}{dt} (\text{mol/m}^3\text{-s}) = \frac{(aF_{\text{air},i} + m_{\text{in},i}u - \Phi_{\text{out}}c_i)}{Q} - k_{\text{deg},i}c_i - \frac{c_i}{Q} \frac{dQ}{dt}, \quad (2)$$

where  $a = wu$  ( $\text{m}^2/\text{s}$ ) is the stream surface area in contact with atmosphere corresponding to 1 second's worth of flow;  $F_{\text{air},i}$  ( $\text{mol}/\text{m}^2\text{-s}$ ) is the net air-water VOC flux and may be positive or negative if the stream is under- or supersaturated, respectively, with respect to the local atmospheric VOC concentration;  $m_{\text{in},i}$  ( $\text{mol}/\text{m}\text{-s}$ ) is differential input rate for  $i$  given as the mass inflow in terms of moles per unit time per distance along the river from local point sources, or from ground-water inflow (but not from the atmosphere, which is considered separately by the term  $aF_{\text{air},i}$ );  $\Phi_{\text{out}}$  ( $\text{m}^3/\text{s}^2$ ) is differential rate at which stream-water discharge is lost by water outflow to ground water or to a point withdrawal ( $\Phi_{\text{out}}$  is "positive-definite": it can be positive or zero, but cannot be negative); and  $k_{\text{deg},i}$  ( $1/\text{s}$ ) is first-order degradation rate constant for  $i$ . The term  $(c_i/Q)(dQ/dt)$  accounts for changes in  $c_i$  due to changes in  $Q$  alone.

As described in Pankow and others (2006), there are two complementary approaches for calculating  $F_{\text{air},i}$ . In the first method,  $F_{\text{air},i}$  is calculated as a net flux using the relation

$$F_{\text{air},i} = k_{\text{OL},i}(c_{\text{s},i} - c_i), \quad (3)$$

where  $k_{\text{OL},i}$  ( $\text{m}/\text{s}$ ) is the local air-water mass transfer velocity of  $i$ , and  $c_{\text{s},i}$  is the saturation concentration of the volatile species with respect to Henry's Gas Law. Using the net flux approach, the atmosphere is a source of VOC only when the concentration difference,  $(c_{\text{s},i} - c_i)$ , is positive; when the concentration difference is zero or negative, the atmosphere is not a source of VOC.

The second method is called the component flux method and, in this case  $F_{\text{air},i}$  is calculated as the difference between the

#### 4 StreamVOC—A Deterministic Source-Apportionment Model to Estimate VOCs in Rivers and Streams

absorptive flux into the stream,  $J_{\text{abs}}$ , and the volatilization from the stream,  $J_{\text{vol}}$ . The absorptive flux is calculated as

$$J_{\text{abs}} = k_{\text{OL},i} c_{\text{s},i} , \quad (4)$$

and  $J_{\text{vol}}$  is given by

$$J_{\text{vol}} = k_{\text{OL},i} c_i , \quad (5)$$

so that as long as the partial pressure of the VOC in the atmosphere is not equal to zero, the air is a source of VOC to the stream.

The change in  $Q$  with time,  $dQ/dt$ , is calculated internally by StreamVOC based on position-dependent user inputs for  $h$ ,  $w$ ,  $u$ ,  $\Phi_{\text{out}}$ , and the source flows. Conceptually,  $dQ/dt$  is given by

$$\frac{dQ}{dt} = \phi_{\text{gw}}(t) + \sum_{k=1}^{N_s} \phi_{\text{ps},k} \delta(t-t_k) , \quad (6)$$

where  $\phi_{\text{gw}}(t)$  ( $\text{m}^3/\text{s}$ ) is the ground-water inflow or loss rate to the stream as a function of time,  $\phi_{\text{ps},k}$  ( $\text{m}^3/\text{s}$ ) is the flow volume added by the  $k$ 'th point source (or removed by the  $k$ 'th point withdrawal), and  $\delta(t-t_k)$  is the Kroenecker delta function for time  $t_k$ , or the time that the  $k$ 'th point source enters the stream. In the case where  $\phi_{\text{gw}}(t)$  is positive (that is, ground-water inflow to the stream) the VOC mass inflow to the stream due to the ground water,  $m_{\text{in},i}(\text{GW})$  is defined as

$$m_{\text{in},i}(\text{GW}) = \frac{\phi_{\text{gw}}(t) c_{\text{gw},i}(t)}{u} , \quad (7)$$

where  $c_{\text{gw},i}(t)$  is the ground-water concentration of  $i$  at time  $t$ . In the case where  $\phi_{\text{gw}}(t)$  is negative,  $\Phi_{\text{out}} = -\phi_{\text{gw}}(t)$ . For  $\phi_{\text{ps},k}$ , the point-source VOC mass inflow to the stream,  $m_{\text{in},i}(\text{PS})$ , is equal to

$$m_{\text{in},i}(\text{PS}) = \frac{\phi_{\text{ps},k} c_{\text{ps},i,k} \delta(t-t_k)}{u} , \quad (8)$$

where  $c_{\text{ps},i,k}$  is the concentration of  $i$  in point source  $k$ . In the case where  $\phi_{\text{ps},k}$  is a point withdrawal,  $\Phi_{\text{out}} = \phi_{\text{ps},k}$ .

The source apportionment fractions for the  $j$  sources (where  $j$  equals the sum of the number of discrete ground-water sources and the  $k$  point sources) are readily calculated from the equations for  $c_i$ ,  $M_i$ , and  $Q$  given previously (equations 1 and 2). Differentiation of equation 1 yields

$$\frac{d\alpha_{i,j}}{dt} = \frac{1}{M_i} \left( \frac{dM_{i,j}}{dt} - \alpha_{i,j} \frac{dM_i}{dt} \right) , \quad (9)$$

where the units of both  $dM_{i,j}/dt$  and  $dM_i/dt$  are  $\text{mol}/\text{s}^2$ . During execution, only the atmosphere and one additional source  $j$  at a time is considered in the model. The functional form depends slightly on whether the net flux or component flux method is being used. For the net flux method and the atmosphere being a source of a VOC to the stream (for example, invasion,  $F_{\text{air},i} > 0$ ),  $dM_{i,j}/dt$  for source  $j$  is calculated by

$$\frac{dM_{i,j}}{dt} = m_{\text{in},i} u - \alpha_{i,j} (\Phi_{\text{gw}} c_{\text{gw},i} + k_{\text{deg},i} c_i Q) , \quad (10)$$

and when the atmosphere is a sink of VOC (for example, evasion,  $F_{\text{air},i} < 0$ ),  $dM_{i,j}/dt$  is calculated by

$$\frac{dM_{i,j}}{dt} = m_{\text{in},i} u - \alpha_{i,j} (\Phi_{\text{gw}} c_{\text{gw},i} + k_{\text{deg},i} c_i Q - a F_{\text{air},i}) . \quad (11)$$

Most importantly, if  $F_{\text{air},i} > 0$  and the atmosphere is a source of a VOC,  $dM_{i,\text{air}}/dt$  is calculated by

$$\frac{dM_{i,\text{air}}}{dt} = a F_{\text{air},i} - \alpha_{i,\text{air}} (\Phi_{\text{gw}} c_{\text{gw},i} + k_{\text{deg},i} c_i Q) , \quad (12)$$

whereas the source fraction for the atmospheric source remains unchanged if the river is losing the VOC to the atmosphere so that  $F_{\text{air},i} \leq 0$ .

In the case of source apportionment calculations using the component flux method, no distinction needs to be made between invasion and evasion, and equations 10 and 11 reduce to

$$\frac{dM_{i,j}}{dt} = m_{\text{in},i} u - \alpha_{i,j} (\Phi_{\text{gw}} c_{\text{gw},i} + k_{\text{deg},i} c_i Q - a J_{\text{vol},i}) \quad (13)$$

for nonatmospheric sources, and the atmospheric source in equation 12 becomes

$$\frac{dM_{i,\text{air}}}{dt} = a J_{\text{abs},i} - \alpha_{i,\text{air}} (\Phi_{\text{gw}} c_{\text{gw},i} + k_{\text{deg},i} c_i Q + a J_{\text{vol},i}) \quad (14)$$

for the atmospheric source. Comparing equations 10 and 11 for the net flux approach with equation 13 for the component flux method and comparing equation 12 (net flux method) with equation 14 (component flux method) shows that when the concentration of VOC in the atmosphere is equal to zero (that is,  $c_s = 0$ ) the two ways of treating the atmospheric source are mathematically identical.

The final relation necessary for application of equation 9 is a relation for  $dM_i/dt$ . Because  $c_i = M_i/Q$ , it can be shown based on equation 2 that

$$\frac{dM_i}{dt} = a F_{\text{air},i} + m_{\text{in},i} u - \Phi_{\text{gw}} c_{\text{gw},i} - k_{\text{deg},i} c_i Q , \quad (15)$$

which can be substituted into equation 9 along with the applicable form for  $dM_{i,j}/dt$  to allow calculation of  $d\alpha_{i,j}/dt$ .

Comparison of the different formulations of the air-water gas flux shows that the main difference between the two methods is in the behavior of the SA. For example, in the net flux method, when  $c_i = c_{\text{s},i}$ , the system is in equilibrium, and there is no change in the SA. Similarly, when  $c_i > c_{\text{s},i}$ , the stream is losing the VOC to the atmosphere, and again there is no change in the SA. In contrast, in the component flux method, whenever  $c_{\text{s},i} > 0$ , the atmosphere is a source of the VOC to the stream, and in the absence of other sources  $\alpha_{i,\text{air}}$  will increase. However, it is important to understand that as far as the change in the total concentration  $c_i$  is concerned, both the net flux method and the component flux method are identical.

Theoretical estimates of air-water gas fluxes at waterfalls (McLachlan and others, 1990) and the results of recent tracer studies (Caplow and others, 2004) have shown that waterfalls and weirs can be dominant mechanisms for air-water exchange

in river systems. As described by Gulliver and others (1998), gas exchange at a hydraulic structure in a stream is given in terms of the transfer efficiency,  $E_i$ , defined as

$$E_i = \frac{(c_{d,i} - c_{u,i})}{(c_{s,i} - c_{u,i})}, \quad (16)$$

where  $c_{u,i}$  is the concentration of the species upstream from the structure, and  $c_{d,i}$  is the concentration downstream from the structure.  $E_i$  is a function of the physical characteristics of the hydraulic structure, the molecular diffusivity of  $i$ , and the solubility of  $i$ .

Regardless of the functional form used for  $E_i$ , air-water exchange of  $i$  at a hydraulic structure in a stream is treated as a step function change in its concentration. The effect this has on the SA is determined by whether the net flux or component fluxes approach is being used.

For the net flux method, in the case where the net flux of  $i$  is from the water to the air (for example, evasion),  $c_{d,i} < c_{u,i}$  as defined by equation 16. In this case, there will be no change in the SAs because all sources were assumed to have lost a proportional fraction based on the assumption that volatilization acts to decrease all of the local  $c_{i,j}$  in proportion to their local  $\alpha_{i,j}$  values (see SA rule 2 given previously in the Introduction section). In the case of net flux of  $i$  from the air to the water (for example, invasion),  $c_{d,i} > c_{u,i}$ . In contrast to evasion, the change in SA for invasion of  $i$  must be calculated because mass of  $i$  was added to the atmospheric source fraction. Assuming that  $Q$  is constant upstream and downstream from the structure, the source fractions for the nonatmospheric sources immediately downstream from the hydraulic structure are

$$\alpha_{d,i,j} = \frac{\alpha_{u,i,j} c_{u,i}}{c_{d,i}}, \quad (17)$$

where  $\alpha_{d,i,j}$  is the SA fraction for source  $j$  immediately downstream from the structure, and  $\alpha_{u,i,j}$  is the SA fraction for source  $j$  immediately upstream from the structure. The SA fraction for the atmospheric source downstream from the structure,  $\alpha_{d,i,\text{air}}$ , can be written as

$$\alpha_{d,i,\text{air}} = \frac{(c_{d,i} - c_{u,i}) + \alpha_{u,i,\text{air}} c_{u,i}}{c_{d,i}}, \quad (18)$$

where  $\alpha_{u,i,\text{air}}$  is the upstream SA fraction for the atmospheric source term of  $i$ .

When the component flux method is being used to estimate  $\alpha_{i,j}$ , SAs must be calculated after aeration by the hydraulic structure for both evasion and invasion. In this case, it is more convenient to define the effect on the SAs in terms of  $E_i$ . The SA downstream from the hydraulic structure of the nonatmospheric sources is defined as

$$\alpha_{d,i,j} = \alpha_{u,i,j} \left[ \frac{c_{u,i}(1 - E_i)}{c_{d,i}} \right], \quad (19)$$

which applies for both invasion and evasion. Similarly,  $\alpha_{d,i,\text{air}}$  is equal to

$$\alpha_{d,i,\text{air}} = \frac{\alpha_{u,i,\text{air}} c_{u,i} (1 - E_i) + E_i c_{s,i}}{c_{d,i}}, \quad (20)$$

which applies to both invasion and evasion.

Substantial flow of water under the hydraulic structure is possible, which will decrease the apparent aeration efficiency of the structure and change the relations given previously for SA. Darcy's Law relates the flow under a structure to the hydraulic conductivity and hydraulic head as

$$Q_{\text{under}} = \frac{\kappa SH}{d}, \quad (21)$$

where  $Q_{\text{under}}$  ( $\text{m}^3/\text{s}$ ) is the flow underneath the hydraulic structure,  $\kappa$  ( $\text{m/s}$ ) is hydraulic conductivity,  $S$  ( $\text{m}^2$ ) is cross-sectional area for flow under the structure,  $H$  ( $\text{m}$ ) is total hydraulic head or pressure gradient, and  $d$  ( $\text{m}$ ) is depth of flow under the structure. The effect of  $Q_{\text{under}}$  on aeration can be viewed in terms of dilution, where the flow over the structure (for example,  $Q - Q_{\text{under}}$ ) has its VOC concentration changed as specified by equation 16 and the flow under the structure has no change in VOC concentration. These two waters are assumed to mix completely downstream from the structure so that  $c_i$  immediately downstream from the structure can be written as

$$c_i = \frac{c_{u,i} Q_{\text{under}} + c_{d,i} (Q - Q_{\text{under}})}{Q}, \quad (22)$$

where  $c_{d,i}$  is the VOC concentration in the water that flowed over the weir as calculated using equation 16.

The effect of this flow on SA can be expressed in terms of the fraction of the total flow going over the structure,  $F_{\text{over}}$ , which is defined as

$$F_{\text{over}} = \frac{Q - Q_{\text{under}}}{Q}. \quad (23)$$

The relations for the change in SA are as follows: equation 17 is unchanged when flow under the weir is taken into account; however, equations 18–20 become

$$\alpha_{d,i,\text{air}} = \frac{F_{\text{over}}(c_{d,i} - c_{u,i}) + \alpha_{u,i,\text{air}} c_{u,i}}{c_{d,i}}, \quad (24)$$

$$\alpha_{d,i,j} = \alpha_{u,i,j} \left[ \frac{c_{u,i}(1 - F_{\text{over}} E_i)}{c_{d,i}} \right], \quad (25)$$

and

$$\alpha_{d,i,\text{air}} = \frac{\alpha_{u,i,\text{air}} c_{u,i} (1 - F_{\text{over}} E_i) + F_{\text{over}} E_i c_{s,i}}{c_{d,i}}, \quad (26)$$

respectively.

Equations 2, 6, 9, and 15 comprise a set of coupled differential equations (DEQs) that can be solved by numerical integration based on data inputs for the stream characteristics by zone, and data inputs for the strengths and locations of the sources acting on the stream. In the following sections of the report, it will be assumed that all flows are steady, all sources and sinks are steady, and vertical/lateral mixing is complete at each point along the length of the stream. For each VOC  $i$ , these assumptions simplify the functionality of each  $c_i(x,y,z,t)$  to  $c_i(x)$ , and simplify the functionalities of each  $\alpha_{i,j}(x,y,z,t)$  to  $\alpha_{i,j}(x)$ .

## Physicochemical Parameterizations

The air-water transfer velocity,  $k_{OL,i}$ , controls the kinetic rate of transfer of  $i$  across the air/water interface. Values of  $k_{OL,i}$  were estimated using the “two-film model” (Liss and Slater, 1974) of air-water gas transfer in which it is postulated that  $k_{OL,i}$  is determined by diffusion-limited molecular transfer through two thin, stagnant layers. One of those layers is on the water side, and the other is on the air side. According to that model,

$$\frac{1}{k_{OL,i}} = \frac{1}{k_{L,i}} + \frac{RT_w}{H_i k_{G,i}}, \quad (27)$$

where  $k_{L,i}$  (m/s) is the mass transfer velocity for  $i$  through the water-side layer,  $k_{G,i}$  (m/s) is the mass transfer velocity for  $i$  through the air-side layer,  $R$  ( $\text{m}^3\text{-atm/K-mol}$ ) is the universal gas constant,  $T_w$  (K) is the water temperature, and  $H_i$  ( $\text{m}^3\text{-atm/mol}$ ) is the Henry’s Gas Law constant for  $i$  at  $T_w$ .

StreamVOC estimates  $k_{L,i}$  values based on estimated values of  $k_2^{20}$  ( $\text{day}^{-1}$ ), which is the rate constant for air-water transfer of oxygen at  $20^\circ\text{C}$  ( $T_w = 293.15$  K). For streams where the overall depth is greater than 0.274 m and less than 11.3 m and the flow velocity is greater than 0.058 m/s and less than 1.28 m/s,  $k_2^{20}$  can be estimated according to the following equation (O’Conner and Dobbins, 1958):

$$k_2^{20} = 3.93 \frac{u^{0.5}}{h^{1.5}}, \quad (28)$$

In the case of streams with  $0.274 \text{ m} > h > 0.119 \text{ m}$  and  $u > 0.04 \text{ m/s}$ , the relation of Owens and others (1964) is used. It has the same functional form as equation 28, but the constant is 6.92 instead of 3.93, the exponent for  $u$  is 0.73 instead of 0.5, and the exponent for  $h$  is 1.75 instead of 1.5. For streams with  $u < 0.04 \text{ m/s}$  and  $h > 0.119 \text{ m}$ , gas transfer is assumed to be driven by wind stress, and  $k_{L,i}$  is calculated using the wind speed relation of Wanninkhof and others (1991). This is

$$k_L = 1.25 \times 10^{-6} \sqrt{\frac{600D_i}{\nu}} U^{1.64}, \quad (29)$$

where  $k_L$  is given in m/s,  $\nu$  is the kinematic viscosity of water in  $\text{cm}^2/\text{s}$  (for  $D_i$  in  $\text{cm}^2/\text{s}$ ), and the wind speed,  $U$ , is in m/s. Although the Wanninkhof and others (1991) relation is defined in terms of  $U_{10}$ , which is the wind speed measured at a height of 10 m for neutral atmospheric stability, it is understood that values for  $U_{10}$  will not be available for most applications of StreamVOC. In these cases, measurements of wind speed made at heights other than 10 m can be used without substantial loss in accuracy of the model. StreamVOC prohibits using stream depths less than 0.119 m, regardless of  $u$ .

StreamVOC corrects  $k_2^{20}$  values to any temperature  $\theta$  ( $^\circ\text{C}$ ) using the following equation (Rathbun, 2000):

$$k_2^\theta = k_2^{20} (1.0241)^{\theta - 20}, \quad (30)$$

where  $\theta$  is equal to  $T_w - 273.15$ . Values of  $k_{L,i}$  are obtained by the following equation (Rathbun, 2000):

$$k_{L,i} = \frac{2.52h(\bar{V}_i)^{-0.301}k_2^\theta}{86400}, \quad (31)$$

where  $\bar{V}_i$  ( $\text{cm}^3/\text{mol}$ ) is the molar volume of  $i$ .

StreamVOC estimates  $k_{G,i}$  values based on the rate constant for air-water transfer of water itself, the molecular weight  $MW_i$  (g/mol), the wind speed  $U$  (m/s), and  $T_A$  ( $^\circ\text{C}$ ) according to the following equation (Rathbun, 2000):

$$k_{G,i} = \frac{4.42 MW_i^{-0.462} (416 + 156 U) \exp[0.00934(T_A - 26.1)]}{86400}. \quad (32)$$

The quantity that acts together with  $k_{OL,i}$  to determine the air-water flux of  $i$  (see equation 2) is

$$\Delta c_i = c_{s,i} - c_i. \quad (33)$$

As previously stated,  $c_{s,i}$  is the water concentration of  $i$  that would be present at  $T_w$  under the condition of “saturation” equilibrium by Henry’s Gas Law with the gas-phase pressure  $p_i$  (atm) in the local ambient air. This Henry’s Gas Law saturation equilibrium concentration is determined from

$$c_{s,i} = \frac{p_i}{H_i}, \quad (34)$$

where

$$p_i = f_i \frac{P}{10^9}, \quad (35)$$

with  $f_i$  (parts per billion by volume, ppbv) equal to the  $i$ -related fraction of the local total ambient atmospheric pressure  $P$  (atm). Recently, for ambient urban air in the United States, Pankow and others (2003) determined that  $f_i < 10$  ppbv for most contaminant VOCs of interest. (For nitrogen in the earth’s atmosphere,  $f_{N_2} = 0.78 \times 10^9$  ppbv.)

StreamVOC can accept user-supplied,  $T_w$ -dependent  $H_i$  values. It also can calculate  $H_i$  values based on  $T_w$  and either the polynomial relation of Wanninkhof (1992), or the following exponential expression (Reid and others, 1987; Rathbun, 2000):

$$H_i(T_w) = \exp\left[A_i - \frac{B_i}{T_w}\right], \quad (36)$$

where  $A_i$  and  $B_i$  are compound dependent constants. An advantage of equation 36 is that  $A_i$  and  $B_i$  values are available for many compounds of environmental interest (Rathbun, 2000).

Relations for  $E_i$ , as defined in equation 16, are available for sharp-crested weirs, ogee-crested weirs, and gated spillways (Gulliver and others, 1998). In general,  $E_i$  is not known for particular VOCs and must be estimated from the transfer efficiency of oxygen measured at 293.16 K. In the case of a sharp-crested weir, the transfer efficiency of oxygen at 293.16 K,  $E_{20}$ , is given by Avery and Novak (1978) as

$$E_{20} = 1 - \left( \frac{1}{1 + 0.24 \times 10^{-4} \mathbf{F}^{1.79} \mathbf{R}^{0.53}} \right)^{1.115}, \quad (37)$$

where  $\mathbf{F}$  and  $\mathbf{R}$  are the Froude and Reynolds numbers, respectively, of the flow over the hydraulic structure.  $\mathbf{F}$  is expressed in terms of the specific flow of the stream over the weir as

$$\mathbf{F} = \left( \frac{8g\eta^3}{q^2} \right)^{1/4}, \quad (38)$$

where  $g$  ( $\text{m/s}^2$ ) is the acceleration of gravity,  $\eta$  (m) is the head loss across the structure, and  $q$  ( $\text{m}^2/\text{s}$ ) is the specific flow over the weir (defined as  $Q$  divided by the width of the weir).  $\mathbf{R}$  is defined in terms of  $q$  as  $q/\nu$ , where  $\nu$  ( $\text{m}^2/\text{s}$ ) is the kinematic viscosity of water at 293.16 K. In the case of an ogee-crested weir,  $E_{20}$  is given by Rindels and Gulliver (1991) as

$$E_{20} = 1 - \exp\left(\frac{-0.263\eta}{1 + 0.215q} - 0.203h_T\right), \quad (39)$$

where  $h_T$  (m) is the depth of the weir tailwater. The transfer efficiency of a gated spillway (Wilhelms, 1988) is defined as

$$E_{20} = 1 - \exp\left(-0.0086\frac{\eta q}{s} - 0.118\right), \quad (40)$$

where  $s$  (m) is the submergence depth of the gate lip.

Following Urban and others (2001),  $E_{20}$  is converted to the equivalent transfer efficiency for the VOC  $i$  at the system water temperature  $T_w$  using:

$$E_i = 1 - (1 - E_{20})^f, \quad (41)$$

where  $E_i$  is the transfer efficiency of  $i$ , and  $f$  is a compound and temperature specific correction factor given by

$$f = \left(\frac{D_i}{D_{O_2}}\right)^{1/2} [1.0 + 0.02103(T_w - 293.16) + 8.261 \times 10^{-5}(T_w - 293.16)^2], \quad (42)$$

where  $D_{O_2}$  is the molecular diffusivity of oxygen in water at 293.16 K, and  $D_i$  is the diffusivity of  $i$  in water at the water temperature  $T_w$ .

McLachlan and others (1990) have shown that the transfer efficiency of  $i$  at a waterfall also is a function of its solubility. Therefore,  $E_i$  calculated using equation 40 represents the efficiency of a hypothetical VOC with diffusivity equal to  $D_i$  but the solubility of oxygen at 293.16 K. If the solubility of  $i$  is very much different from that of oxygen,  $E_i$  must be corrected for the change in  $H_i$  based on the relations presented by McLachlan and others (1990). From those relations, it can be shown that for  $E_i$  corrected to account for changes in solubility,  $E_i(H_i)$  is approximately equal to

$$E_i(H_i) = 1 - \frac{1}{r_{Hi}}, \quad (43)$$

where  $r_{Hi}$  is defined as:

$$r_{Hi} = \left(r + \frac{RT_w}{150H_i}\right) \left(1 + \frac{RT_w}{150H_i}\right)^{-1} \quad (44)$$

and  $r$  is the gas concentration deficit defined by  $r = 1/(1 - E_i)$  (McLachlan and others, 1990).

Flow under any hydraulic structure through the hyporheic zone is parameterized as a “worst-case” estimate using a hydraulic conductivity of 0.01 m/s, which is the value typical of coarse gravel. For most reasonable values of  $S$  (cross-sectional area for flow through the hyporheic zone),  $H$ , and  $d$  (depth of flow through the hyporheic zone), this results in approximately 20 percent of the total flow going under the structure rather than over the top. Rather than add additional complexity to the model by explicitly calculating  $Q_{\text{under}}$ , it has been assumed that it will be  $0.2Q$  for all structures in the stream. Therefore, the maximum expected effect of aeration by dams and weirs can be turned on and off by a simple flag in the model.

## Model Operation and Numerical Methods

StreamVOC is written in Fortran 90 (Appendix 1) and uses a fourth-order Runge-Kutta integration subroutine (Hall and Watt, 1976) to solve the governing set of coupled DEQs (equations 2, 6, 9, and 15). In this model, each stream zone is discretized into 400 subzones. Within each subzone,  $Q$  is allowed to vary with distance  $x$ , but only linearly. The average velocity for the subzone  $\bar{u}_{sz}$  (m/s) thus is computed as the velocity at the subzone starting point. The overall time interval for integration over each subzone is determined as  $\Delta x_{sz}/\bar{u}_{sz}$ , where  $\Delta x_{sz}$  (m) is the length of the subzone. The final  $c_i$  and  $\alpha_{i,j}$  values from the integration over a given subzone serve as the initial values for the next subzone.

A large change in flow over a subzone (with or without  $i$ ) can cause instability in the numerical integration of equations 2, 6, 9, and 15. Therefore, StreamVOC distributes each point-source flow over a stream length,  $\Delta x_{ps}$ , equal to the minimum of the local stream width  $w$  or 5 m. Each point-source flow thus begins at zero at the upstream end of  $\Delta x_{ps}$ , is constant over the distance defined by  $\Delta x_{ps}$ , then decreases back to zero at the downstream end of  $\Delta x_{ps}$ . The total flow added over  $\Delta x_{ps}$  equals the flow of the point source. StreamVOC treats the change in flow due to a distributed (“nonpoint”) source (or sink) flow that acts over a stream interval much larger than  $w$  (or 5 m) in an identical manner, where the differential change in flow is constant over the source region.

The effect of weirs and spillways on VOC concentrations and their SAs was calculated as described previously using equations 16–20 and 37–43. StreamVOC treats the decrease or increase in  $c_i$  as an instantaneous event that happens at the end of the subzone containing the hydraulic structure. Under this assumption, the concentration calculated at the end of a subzone containing a hydraulic structure is modified according to the equations described previously. In the case of VOC transfer from the atmosphere to the water at the structure, the source apportionments also are changed instantaneously. These new values are then used to initialize the Runge-Kutta algorithm at the start of the next subzone.

## User Instructions and Information Needs for Running StreamVOC

StreamVOC has been tested using Microsoft Windows 9x, Windows NT 4.0, and Windows 2000/XP. It can be installed to run using a shortcut from the desktop, double clicking on the file StreamVOC.exe in Windows Explorer, or from the Start/Program/Run menu. Apart from copying the executable file to a particular location, no other installation steps are required for StreamVOC.

The data used to initialize and run StreamVOC are entered through an ASCII parameter file, an example of which for modeling methyl *tert*-butyl ether (MTBE) in a 4-km-long section of a hypothetical stream is shown in figure 2. The menu item for reading a parameter file is found under the File menu heading. StreamVOC cannot be run until an error-free parameter file has been read in through the File menu.

The general structure of the parameter file is given in an explanatory comment line that serves as a reminder to the user of the data required and its format followed by one or more lines of input data. The parameter file may be generated using any ASCII-based text editor. In general, word processors should not be used to generate the parameter files due to the presence of embedded codes and non-ASCII text format in the resulting file.

The first two lines of the parameter file set values for three flags related to the operation of StreamVOC. The first flag determines whether the model uses the net flux method or the component flux method to calculate the atmospheric SA term (flag = 0 will cause model to use net flux method, flag = 1 will cause model to use component flux method). The second flag determines whether or not there is water flowing under hydraulic structures (flag = 0 means no water flowing hydraulic structures, flag = 1 will have 20 percent of flow going under hydraulic structures). The third flag instructs the model to expect that streamflow values will be entered in units of cubic meters per second (flag = 0) or cubic feet per minute (flag = 1). The values of these flags must be either zero or one, all three must be present, and their order is not interchangeable.

The next six lines of the parameter file contain the total stream length  $L$  (km), the number of zones, and the number of distributed sources/sinks. Zone boundaries are defined as locations where there are point sources of VOCs, tributaries, changes in river depth  $h$  (m), changes in river width  $w$  (m), or changes in streamflow  $\Delta Q$  ( $\text{m}^3/\text{s}$ ). The next section of the parameter file contains the stream physical data in tabular form. The first line in the table gives the initial stream conditions. Subsequent lines of the table list the data for zone boundaries, point sources, or distributed source/sink regions. The structure of each line is Index Number, Start, Stop,  $h$ ,  $w$ ,  $\Delta Q$ , and the VOC concentration in any sources ( $\mu\text{g}/\text{L}$ ). In the case of a zone boundary or a point source, Start = Stop, and in the case of a distributed source, Start < Stop. Furthermore, the Stop location of a distributed source cannot be greater than the Start location of the subsequent zone boundary or distributed source (that is, distributed sources cannot overlap zone boundaries or other distributed sources).

In the example shown in figure 2,  $L = 4.000$  km, and there are four zones and three distributed source regions in the stream. The first line of the stream physical data table shows that initially  $h = 0.30$  m,  $w = 5.0$  m,  $Q = 0.354$   $\text{m}^3/\text{s}$ , and  $c_i = 0.75$   $\mu\text{g}/\text{L}$ . The second line of the table shows that a distributed source starts at  $x = 0.000$  km and continues until  $x = 1.000$  km. The total flow added to the stream by this source is  $0.035$   $\text{m}^3/\text{s}$  so that the rate of change of  $Q$  due to this source would be  $0.035$   $\text{m}^3/\text{s}\cdot\text{km}$ . Finally, the source has a VOC concentration of  $1.25$   $\mu\text{g}/\text{L}$ . The third line shows the zone boundary between the first and second zones. At this boundary,  $h$  increases from  $0.30$  to  $0.50$  m,  $w$  increases from  $5.0$  to  $8.0$  m, and there is no change in  $Q$ . The fourth line is the zone boundary between the second and third zones. Here,  $h$  increases from  $0.50$  to  $0.75$  m with no change in either  $w$  or  $Q$ . The fifth line defines the second distributed source, which is an area of ground-water recharge as  $\Delta Q < 0$ . The sixth line defines the boundary between the third and fourth zones and shows that  $h$  decreases from  $0.75$  to  $0.50$  m with  $w$  remaining constant at  $8.0$  m. However, in contrast to the previous two zone boundaries, the boundary between the third and fourth zones also is a point source (or confluence) where there is a  $\Delta Q$  of  $0.189$   $\text{m}^3/\text{s}$  and an incoming VOC concentration in this flow of  $2.50$   $\mu\text{g}/\text{L}$ . The eighth and final line in the stream physical data table is the end point of the stream to be modeled. The Start location in the final line must be equal to  $L$ , and the other data in this line are unused by StreamVOC.

In the case of distributed and point sources,  $\Delta Q$  is allowed to be positive or negative. However, all other values in the physical data table must be greater than or equal to zero.

The 10 lines of the parameter file after the stream physical data table contain the environmental data for the stream, including water temperature  $T_w$  ( $^{\circ}\text{C}$ ), air temperature  $T_A$  ( $^{\circ}\text{C}$ ), mean wind speed  $U$  (m/s), relative humidity (percent), and local atmospheric (barometric) pressure  $P$  (atm). All five of these values are assumed to be constant over the entire stream.

Following the environmental data, the next 14 lines are used to enter the physicochemical data for the VOC to be modeled. The first data item for the VOC is its atmospheric concentration,  $f_i$  (ppbv), entered here as its atmospheric mixing ratio. The second item is the molecular weight of the VOC,  $MW_i$  (g/mol). Diffusivity is parameterized in StreamVOC using the molar volume-based relation of Wilke and Chang (1955). The molar volume of the VOC at its normal boiling point  $\bar{V}_i$  ( $\text{cm}^3/\text{mol}$ ), the fourth item, can be entered directly or it can be entered as the density of the liquid in grams per cubic centimeter on the flag in the third item. The aqueous-phase solubility of the VOC, the sixth item, is parameterized in terms of the Henry's Gas Law constant  $H_i$  ( $\text{m}^3\text{-atm}/\text{mol}$ ). This can be entered in one of three ways indicated by the appropriate flag in the fifth item. First, it may be entered using the two-parameter exponential relation given in equation 36. Secondly, the five-parameter polynomial expression from Wanninkhof (1992) may be used. The third way is to calculate it externally from StreamVOC and enter that value directly. The final VOC physicochemical data item required is the biochemical degradation rate  $k_{\text{deg}}$  (1/s), which is optional and may be set to zero for no degradation.

The tolerance parameter for the Runge-Kutta routine is related to the precision of the answer. In general, the number of significant digits of the answer,  $N$ , can be selected by choosing the value of the tolerance to be equal to  $10^{-N}$ . However, there is a limit to this relation so that at some point increasing  $N$  will have no appreciable effect on the answer. Users can verify that this is true by running StreamVOC successively with the tolerance set at  $10^{-N}$  and  $10^{-N-1}$ . If smaller values of the parameter

produce no change in the model output, it may be assumed that further decreases will have no effect on model performance.

The next four lines are a parameter file header line and three lines of text that permit the user to annotate a particular model run with a title and as many as two lines of comments describing model conditions. There is a 72-character limit for the title and comment lines.

```
Flux method (0=Net, 1=Component): Weir Flow (0=off, 1=on): Units (0=cubic meters per
second, 1=cubic feet per minute)
  1      0      0
Total Length of River (km)
  4.000
Number of reaches
  4
Number of distributed source regions
  3
River profile/source data (# of points = # of reaches + # of distributed
sources + 1)
#   Start(km)   Stop(km)   Depth(m)   Width(m)   Flow(m3/s)   Conc. (ug/L)
1     0.0         0.0         0.30        5.0         0.354         0.75
2     0.0         1.000        0.30        5.0         0.035         1.25
3     1.000       1.000        0.50        8.0         0.0           0.00
4     2.000       2.000        0.75        8.0         0.0           0.00
5     2.000       3.000        0.75        8.0        -0.012         0.00
6     3.000       3.000        0.50        8.0         0.189         2.50
7     3.000       4.000        0.50        8.0         0.047         0.00
8     4.000       4.000        0.50        8.0         0.047         0.00
River temperatures (C)
  22.00
Air temperature (C)
  20.0
Mean wind speed (m/s)
  4.0
Relative Humidity
  0.80
Barometric pressure (atm)
  1.00
Atmospheric VOC concentration (ppbv)
  0.5
VOC molecular weight in g/mole
  88.15
Index for molar volume data entry (1 for m.v., 2 for density)
  1
Molar Volume at B.P. (cm3/mol) or density (g/cm3)
  129.4
Solubility param (1 for exp(A-B/T), 2 for Wanninkhof, 3 for direct entry)
  1
Solubility Coefficients mol/m3-atm (1: D.E., 2: exp(A-B/T), 5: Wann.)
  0.184000E+02      0.766600E+04
First order VOC biochemical degradation rate (1/s)
  0.0
Tolerance for Runge-Kutta DEQ integrator
  0.1000E-08
Title for run and two lines of comments, comments not used
StreamVOC-Version-2-1;~Sample~Parameter~File
Methyl-t-butyl-ether
This~line~for~additional~comments
waterfall/weir parameterization information
  Number of weirs/waterfalls
  2
Type: 1 = Ogee weir; 2 = sharp-crested weir; 3 = gated sill
Weir#   Location(km)   length   height   silldepth(m)   Tailstockdepth(m)   Type
  1         1.500         4.0     0.9     0.0           1.07                 1
  2         3.250         4.0     0.5     0.0           0.64                 2
d:\streamvoc\output_data\test1.dat
```

Figure 2. Sample ASCII parameter file used by StreamVOC.

The next section of the parameter file allows the user to enter the locations and types of weirs, waterfalls, or hydraulic structures present in the stream. After two initial text lines that denote the beginning of the weir setup data entry, the first parameter is the number of weirs or structures. The weir number is followed by two more text lines, then the table containing the information for each structure in the stream. There must be one line in the table for each structure. The format of each line of the table is the structure index, the location of the structure from the beginning of the stream (km), the length of the structure (m), the height of the structure (m), the sill depth (m) if applicable, the tailstock depth (m) if applicable, and a numerical index defining the type of structure. As shown in figure 2, the Type index can take on the values 1 for an ogee-crested weir, 2 for a sharp-crested weir, and 3 for a gated spillway. The presence of the hydraulic structure portion of the parameter file is optional unless entry of the optional filename for model data output also is desired.

The final line in the parameter file is an optional filename for output of the model data. This option should be used with caution because if this filename is included in the parameter list, StreamVOC will overwrite any existing data file with the same name. Also, the user is responsible for ensuring that any directory path included with the filename is valid. If the user wishes to use this feature and there are no hydraulic structures in the stream, the parameter file must include the two text lines that start the hydraulic structure information portion, a line giving the number of hydraulic structures as zero, and the two text lines preceding the table containing the hydraulic structure information. Because there will be no entries in this table, the data output filename will follow immediately after these two lines of text. The output interval is one data point per subzone and cannot be altered by the user. Alternatively, the drive, directory, and file to which the data are written can be set by the 'Save VOC Model Results' option under the "File" menu in the main window of StreamVOC. If a model run is initiated without an output filename specified, the user will be notified that the results will not be saved to disk.

Inconsistencies or nonrealistic values (that is, VOC concentrations  $< 0$ ) in the parameter file will be flagged in an error display window. The parameter file must be modified externally from StreamVOC to correct these errors and re-read into StreamVOC from the File/Read Parameter File submenu. Once a parameter file has been entered, the Run and View Parameters submenu options will be enabled. At this point, the input parameters may be examined in the model using the View Parameters menu options. Once it has been determined that the input information is correct, the model is started using the "Start Model" option under the "Run" menu in the main window. Model output to the main screen should begin soon after the run has been started. The user may terminate a model run before the final time using the "Halt Model" option in the "Run" menu. All other menu items are disabled while the model is running.

## Verification of StreamVOC

The performance of StreamVOC was evaluated for numerical accuracy in two ways. First, numerical experiments were conducted using a hypothetical stream where the VOC concentration could be calculated analytically as a function of distance in a study region. By running different scenarios of point and distributed sources, the numerics of the model in regards to dilution, air-water gas exchange, and the SA calculations could be tested. The second set of experiments made use of a source synoptic study data set from the Aberjona River in Winchester, Massachusetts. This data set provided a means to test the performance of the model in estimating measured surface-water concentrations in a more realistic stream.

## Hypothetical Base-Case Stream Using Methyl *tert*-Butyl Ether

The simulations described in this section were carried out using methyl *tert*-butyl ether (MTBE) as the VOC of interest to check the performance of the code. These tests involved a hypothetical base-case stream with  $L = 100$  km,  $w = 5$  m,  $h = 0.5$  m,  $u = 0.4$  m/s,  $Q = 1$  m<sup>3</sup>/s,  $T_w = 20^\circ\text{C}$ ,  $P = 1$  atm, and  $U = 4$  m/s (it should be noted that the example used here does not correspond to the parameter file shown in figure 2). The long and uniform nature of the stream allowed the gas exchange parameterization in the model to be tested by comparing the timescales required for achievement of Henry's Gas Law equilibrium between the stream and the atmosphere to timescales derived from analytical solutions of the relevant DEQs. Equation 36 with  $A_{\text{MTBE}}$  and  $B_{\text{MTBE}}$  from Robbins and others (1993) was used to determine that  $H_{\text{MTBE}}(T_w = 20^\circ\text{C}) = 4.3 \times 10^{-4}$  m<sup>3</sup>-atm/mol.  $\bar{V}_{\text{MTBE}}$  was based on density data (for liquid MTBE) found in the Beilstein CrossFire database BS030200PR at <http://chemistry.library.wisc.edu/beilstein/home.htm>. Sensitivity tests indicated that  $k_{\text{OL},i}$  depends only very weakly on wind velocity  $U$  for many VOCs, even for a relatively soluble VOC such as MTBE.

Mixing/dilution as performed in StreamVOC was examined using two test cases built on the base-case stream. The assumed water and air levels place the base-case stream initially supersaturated with respect to Henry's Gas Law equilibrium for MTBE. For both cases, the MTBE concentration in the inflow to zone 1 ( $x = 0$ ) was assigned as 5.0  $\mu\text{g/L}$ , and  $f_{\text{MTBE}}$  for the atmosphere was assigned as 5.0 ppbv. (For  $H_{\text{MTBE}}(T_w = 20^\circ\text{C}) = 4.3 \times 10^{-4}$  m<sup>3</sup>-atm/mol, 5.0 ppbv corresponds to  $c_{s,\text{MTBE}} = 1.0$  ppbv/( $\mu\text{g/L}$ .) In the first test case, an MTBE-free point flow of 1 m<sup>3</sup>/s was placed at  $x = 1$  km. Immediately upstream from the added flow at  $x = 0.9975$  km, the model simulated MTBE concentration = 4.986  $\mu\text{g/L}$ ; immediately downstream from the added flow at  $x = 1.0005$  km, the model correctly simulated MTBE concentration = 2.493  $\mu\text{g/L}$ . Because there was not enough distance over the point-source region for there to be an



appreciable loss of MTBE due to volatilization, MTBE decreased through dilution by a factor of two as expected. In the second test case, the point-source flow was replaced with a  $1 \text{ m}^3/\text{s}$  MTBE-free distributed flow that extended from  $x = 1 \text{ km}$  to  $2 \text{ km}$ . At  $x = 0.9975 \text{ km}$ , the model simulated MTBE concentration =  $4.986 \text{ }\mu\text{g/L}$ ; at  $x = 2.000 \text{ km}$ , the model simulated MTBE concentration =  $2.488 \text{ }\mu\text{g/L}$ . In this second case, the loss of MTBE through volatilization over the 1-km-long source region causes a small, but noticeable, decrease in MTBE that is in addition to the much larger decrease by dilution. Therefore, the final concentration is less than in the previous example although still approximately a decrease of a factor of two.

SA allocations for the net flux method as performed by StreamVOC also were examined using two test cases built on the base-case stream, and using the same inflow ( $x = 0$ ) water concentration (MTBE concentration =  $5.0 \text{ }\mu\text{g/L}$ ), and the same air level ( $f_{\text{MTBE}} = 5.0 \text{ ppbv}$ ) utilized in the two mixing/dilution test cases. In the first SA test, an added point-source (PS) flow of  $1 \text{ m}^3/\text{s}$  with MTBE concentration =  $5 \text{ }\mu\text{g/L}$  was located at  $1 \text{ km}$ . Immediately upstream from the point source, StreamVOC estimated MTBE concentration =  $4.986 \text{ }\mu\text{g/L}$  with  $\alpha_{\text{INFLOW}} = 1.0$  and  $\alpha_{\text{PS}} = 0.0$ ; immediately downstream from the point source, the model estimated MTBE concentration =  $4.992 \text{ }\mu\text{g/L}$  with  $\alpha_{\text{INFLOW}} = 0.4994$  and  $\alpha_{\text{PS}} = 0.5006$ . Neglecting volatilization losses and accounting only for mixing, the values calculated for MTBE concentration,  $\alpha_{\text{INFLOW}}$ , and  $\alpha_{\text{PS}}$  were  $4.992 \text{ }\mu\text{g/L}$ ,  $0.4993$ , and  $0.5007$ , respectively. In a second SA allocation test, the added source acting along the stream was changed to a distributed flow, nonpoint source (NPS) extending from  $x = 1$  to  $2 \text{ km}$ , with  $1 \text{ m}^3/\text{s}$  of total added flow, and MTBE concentration =  $5.0 \text{ }\mu\text{g/L}$  in that flow. At  $x = 1 \text{ km}$ , the model estimated MTBE concentration =  $4.986 \text{ }\mu\text{g/L}$ ,  $\alpha_{\text{INFLOW}} = 1.0$ , and  $\alpha_{\text{NPS}} = 0.0$ . At  $x = 2 \text{ km}$ , the model correctly estimated MTBE concentration =  $4.983 \text{ }\mu\text{g/L}$ ,  $\alpha_{\text{INFLOW}} = 0.4991$ , and  $\alpha_{\text{NPS}} = 0.5009$ . The slightly larger  $\alpha$  value for the NPS resulted from proportionally more volatilization of the inflow-related MTBE than of the NPS-related MTBE.

SA calculations for the component flux method were tested by observing that when the aqueous-phase VOC concentration is in equilibrium with the atmosphere and the initial source fraction for the atmospheric source is zero, the time evolution of  $\alpha_{i,\text{air}}$  has the closed-form analytical solution

$$\alpha_{i,\text{air}} = 1 - \exp\left(-\frac{k_{\text{OA},i}t}{h}\right). \quad (45)$$

Figure 3 shows  $\alpha_{i,\text{air}}$  calculated by StreamVOC for a stream having the physical characteristics described previously that is in equilibrium with an atmospheric concentration of MTBE of  $5 \text{ ppbv}$ . Figure 3 also shows  $\alpha_{i,\text{air}}$  calculated using the analytical solution in equation 45. There is no substantial difference between the model output and the analytical solution.

Gas transfer as performed in StreamVOC was examined using two test cases built on the base-case stream and the same air level ( $f_{\text{MTBE}} = 5.0 \text{ ppbv}$ ) used previously. For the first test case, the stream was assumed to contain MTBE concentration at  $5.0 \text{ }\mu\text{g/L}$  at  $x = 0$ . Volatilization to the atmosphere would thus

tend to occur until MTBE dropped to  $1.005 \text{ }\mu\text{g/L}$ ; the model simulated MTBE concentration =  $1.006 \text{ }\mu\text{g/L}$  at  $x = 83.208 \text{ km}$ , which is consistent with that expectation. For the second test case, the stream inflow ( $x = 0$ ) was assumed to contain MTBE concentration at  $0.1 \text{ }\mu\text{g/L}$ . Ingassing from the atmosphere would thus tend to occur until MTBE concentration =  $1.005 \text{ }\mu\text{g/L}$ ; the model simulated MTBE concentration =  $1.005 \text{ }\mu\text{g/L}$  at  $x = 70.677 \text{ km}$ .

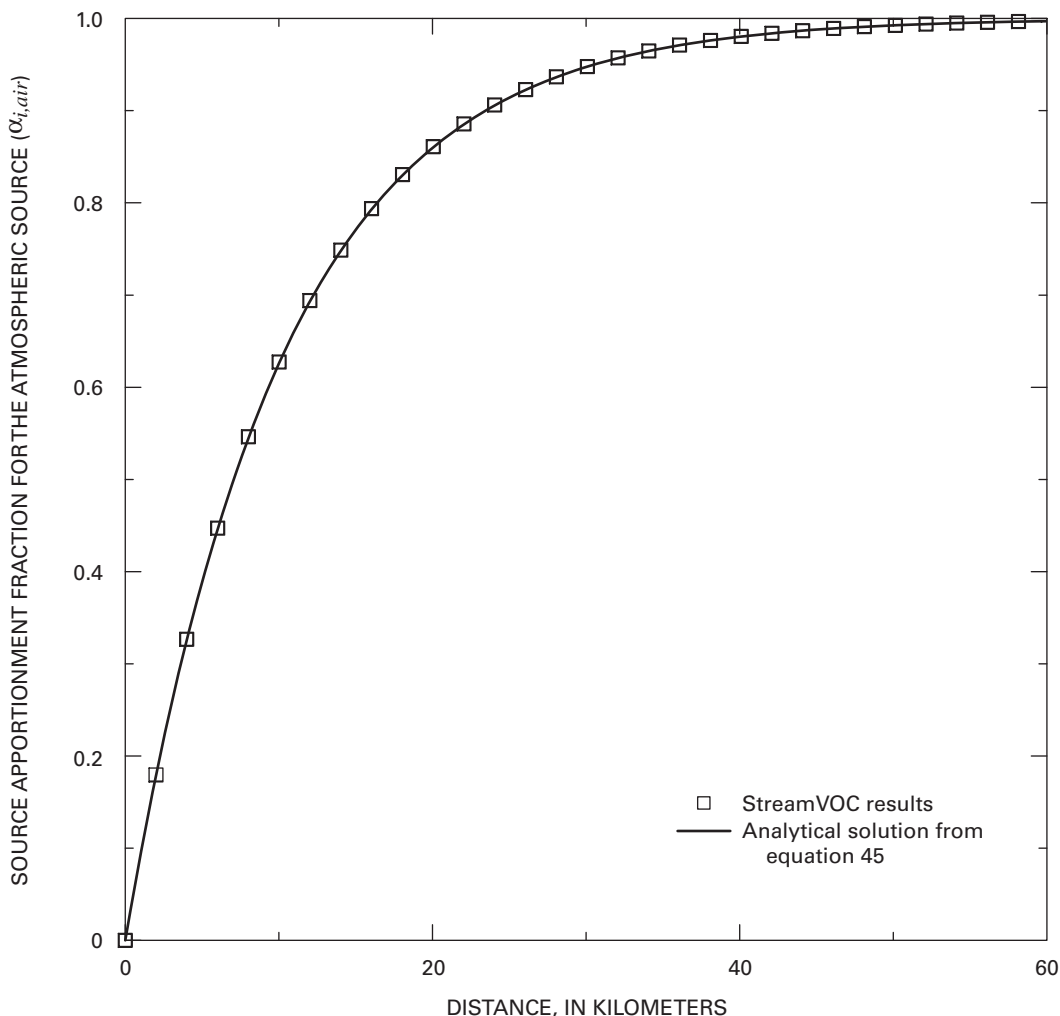
The in-stream loss as calculated by StreamVOC was examined by addition of degradation (with  $k_{\text{deg,MTBE}} = 2 \times 10^{-5}/\text{s}$ ) to the two gas-transfer test cases considered previously. Because  $f_{\text{MTBE}}$  in the atmosphere is not zero for these two cases, the inclusion of constant degradation means that Henry's Gas Law equilibrium can never be reached for either case, even at very large  $x$ . However, at sufficiently large  $x$ , the stream can achieve a steady-state condition for which the local MTBE entry rate into the river balances the local in-stream loss rate by degradation. For the case when the initial MTBE concentration =  $5 \text{ }\mu\text{g/L}$ , the model simulated a steady-state MTBE concentration of  $0.6660 \text{ }\mu\text{g/L}$  for  $x > 80.2 \text{ km}$ . For a parcel of water corresponding to 1 second's worth of flow, the corresponding MTBE entry and loss rates are both  $1.33 \text{ }\mu\text{g/L-s}$ . For the case when the initial MTBE concentration =  $0.1 \text{ }\mu\text{g/L}$ , the same steady-state condition was reached once  $x > 60.150 \text{ km}$ .

The concentrations of MTBE estimated by StreamVOC for the gas exchange test cases described previously can be further evaluated by comparison to the analytical solution of the DEQ for the test system. Because the stream for the validation studies had  $m_{\text{in},i} = 0$ ,  $\Phi_{\text{gw}} = 0$ , and constant  $Q$ ,  $u$ , and  $h$ , integration of equation 2 shows that the concentration at any point  $x$  in the stream,  $c_i(x)$ , is given by

$$c_i(x) = \frac{k_{\text{OL},i}c_{s,i}}{k_{\text{OL},i} + hk_{\text{deg},i}} - \left( \frac{k_{\text{OL},i}c_{s,i}}{k_{\text{OL},i} + hk_{\text{deg},i}} - c_{0,i} \right) x \exp\left[ -\left( \frac{k_{\text{OL},i}}{h} + k_{\text{deg},i} \right) \frac{x}{u} \right], \quad (46)$$

where  $c_0$  is the VOC concentration at the upstream end of the stream. The stream physical conditions used are  $L = 100 \text{ km}$ ,  $w = 5 \text{ m}$ ,  $h = 0.5 \text{ m}$ ,  $u = 0.4 \text{ m/s}$ ,  $Q = 1 \text{ m}^3/\text{s}$ ,  $T_w = 20^\circ\text{C}$ ,  $P = 1 \text{ atm}$ , and  $U = 4 \text{ m/s}$ . From these values, direct calculation of  $k_{\text{OL,MTBE}}$  using the relations in the Physicochemical Parameterizations section found  $k_{\text{OL,MTBE}} = 1.963 \times 10^{-5} \text{ m/s}$ , which is identical to the numerical value produced by StreamVOC.

Figure 4 shows the model simulated MTBE concentration plotted along with the analytical solution shown in equation 46 for air-water transfer with no biochemical degradation (that is,  $k_{\text{deg},i} = 0$ ) for  $c_0 > c_s$  (outgassing) and  $c_0 < c_s$  (ingassing). The model results match the analytical solution to the fourth decimal place, which demonstrates that StreamVOC is correctly calculating the air-water exchange of VOCs for both invasion and evasion when there is no biochemical degradation.



**Figure 3.** Source apportionment fraction for the atmospheric source,  $\alpha_{i,air}$ , of methyl *tert*-butyl ether calculated by StreamVOC for a stream in atmospheric equilibrium using the component flux method for the test stream described in text. Also shown are values for  $\alpha_{i,air}$  calculated using the analytical solution given in equation 45 for the same conditions as used in the model.

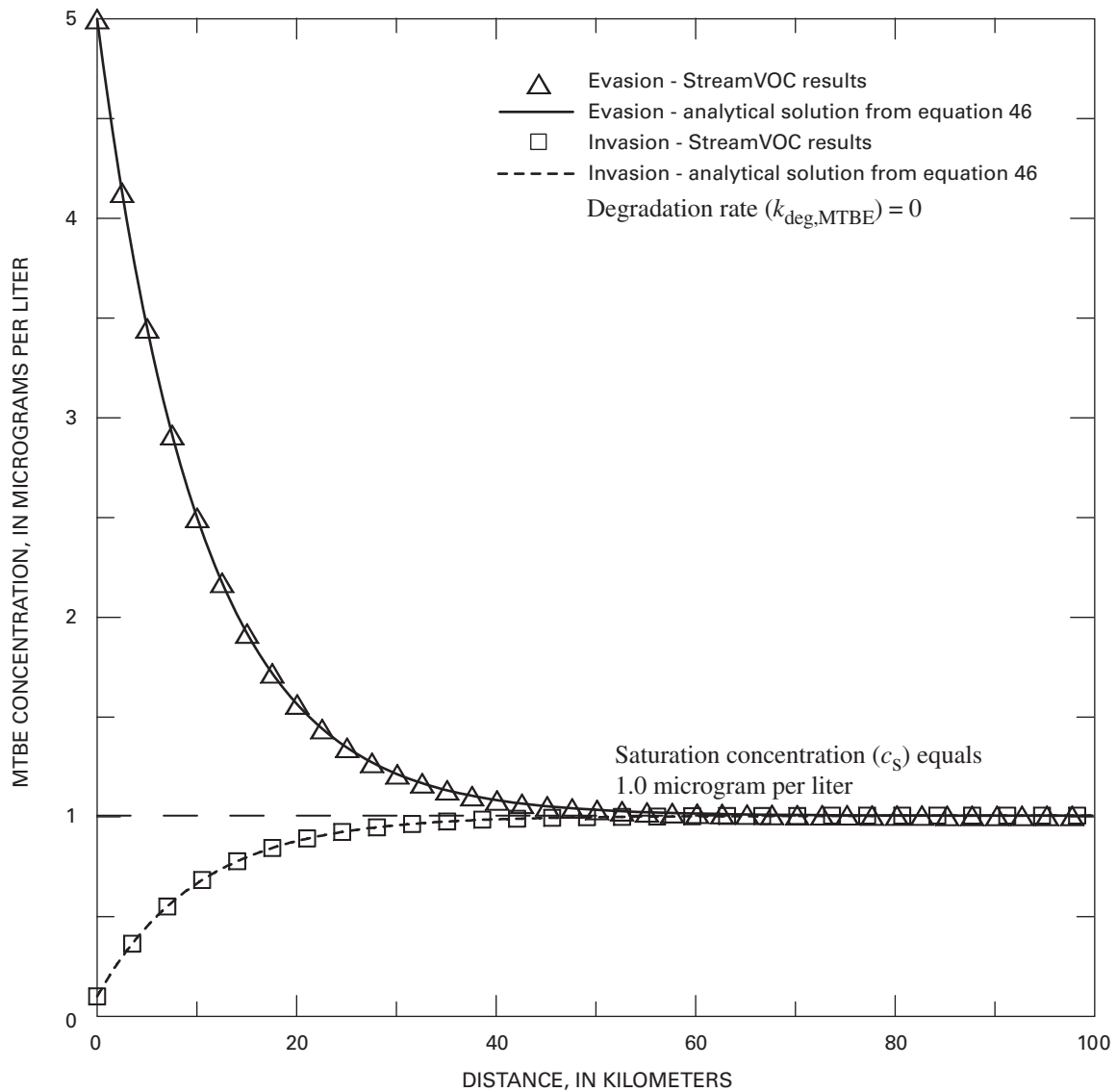
Figure 5 shows the model simulated MTBE concentration plotted along the analytical solution shown previously for air-water transfer with  $k_{deg,MTBE} = 2 \times 10^{-5}/s$  for  $c_0 > c_s$  (evasion) and  $c_0 < c_s$  (invasion). The model results when degradation is included as a VOC loss mechanism also match the analytical solution to the fourth decimal place. The comparisons shown in figures 4 and 5 and discussed in this section demonstrate that the numerical solutions of StreamVOC function correctly.

### StreamVOC Validation Using the Aberjona River

The performance of StreamVOC in modeling concentrations and their SAs in an actual stream was tested using a data set collected on the Aberjona River in Winchester, Massachusetts, for an intensive source-synoptic study during July 11–13, 2001. This section of the report describes the test site and provides modeling results for eight VOCs.

### Study Test Site Description

Depth ( $h$ ), width ( $w$ ), and flow ( $Q$ ) values were measured over a 2.811-km section of the stream on July 11, 2001. Figure 6 and table 1 show that the 2.811-km section was divided into 10 main zones based on stream characteristics. Zone 8 contains two ponds connected by a short channel, and in terms of model parameterization, each pond and the connecting channel were defined as separate subzones in zone 8. The confluence with Horn Pond Brook is located immediately upstream from the boundary between zones 7 and 8a, and for convenience of discussion in this report this confluence is considered to coincide with the zone boundary. The stream zone numbers and distance increase going downstream. Figure 7 shows the average values for  $u$  calculated from  $h$ ,  $w$ , and  $Q$ ;  $Q$  determined from flow measurements; and  $w$  and  $h$  in each zone plotted as a function of distance downstream from the start of the synoptic study



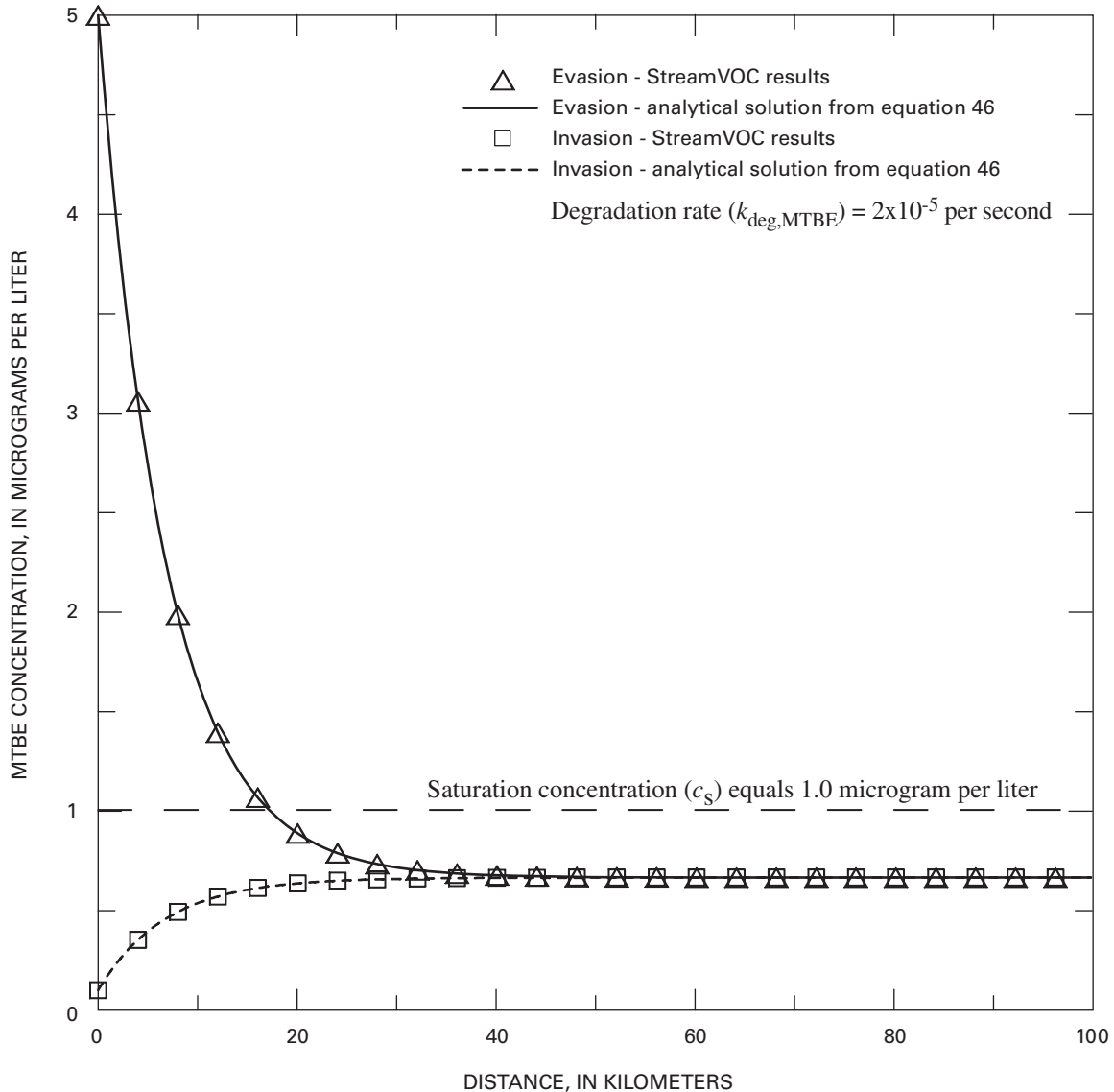
**Figure 4.** Concentration of methyl *tert*-butyl ether (MTBE) calculated by StreamVOC assuming no biochemical degradation for the test stream described in text. Also shown are MTBE values calculated using the analytical solution of equation 2 given in equation 46 for the same conditions as used in the model.

region. The presence of the ponds in zones 8a and 8c reduces  $u$  in these sections to less than 0.04 m/s, and the air-water gas exchange is then driven by wind stress as shown by equation 29.

The hydrogeologic setting of the Aberjona River watershed is typical of what is found in glaciated areas of southern New England—a gentle valley underlain by bedrock and surficial till, sand, and gravel deposits (deLima and Olimpio, 1989). A sand and gravel aquifer is present along the stream course and tapers outward along the slopes of the surrounding hills. North of Winchester in Woburn, Massachusetts, the thickness of this aquifer ranges from zero at the sides of the valley to 140 ft underneath the stream channel (deLima and Olimpio, 1989). This aquifer contains layers ranging from fine sands and silt to coarse sands and gravels. Peat deposits also are adjacent to and underneath the Aberjona River in some locations. A layer of till is beneath the sand and gravel aquifer and is present on the

surface where the sand and gravel deposits are absent. Bedrock outcrops are along the slopes and tops of the valley divide. Ground-water flow generally is downgradient along the valley sides towards the river; the river is a discharge point of ground water. There also is vertical mixing of ground water within the sand and gravel aquifer and between the surficial and bedrock aquifers.

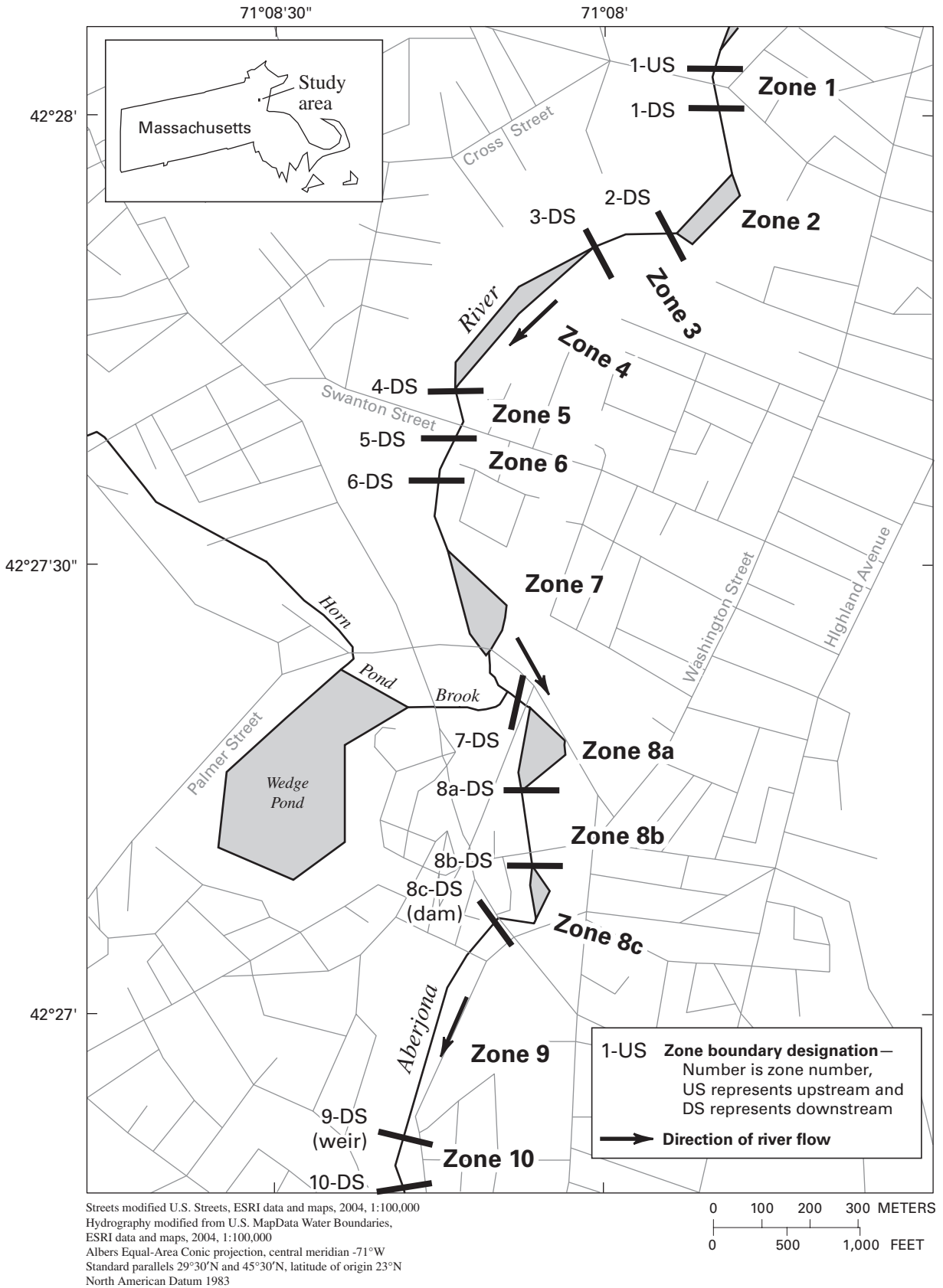
When possible,  $h$  and  $w$  were measured at multiple locations in a zone across the stream in the case of  $h$  and along the stream in the case of  $w$ .  $Q$  was measured at the end of each zone and tracked over the duration of the synoptic study. Surface-water samples were collected on July 11, 2001, between the hours of 0600 Eastern Daylight Time (EDT) and 2000 EDT, during which  $Q$  decreased from 0.680 to 0.596 m<sup>3</sup>/s with a time-weighted average of 0.613 m<sup>3</sup>/s.



**Figure 5.** Concentration of methyl *tert*-butyl ether (MTBE) calculated by StreamVOC assuming a biochemical degradation rate of  $2 \times 10^{-5}$  per second for the test stream described in text. Also shown are MTBE values calculated using the analytical solution of equation 2 given in equation 46 for the same conditions as used in the model.

There are two hydraulic structures in the Aberjona River in the synoptic study region, and their locations are denoted at the top of figure 7. In order of zone number, the first structure is located at the downstream end of zone 8c and is a small stepped dam that was assumed to function 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 dimensions of the dam and weir used in calculating their respective  $E_i(H_i)$  values were determined from photographs taken during the synoptic study measurements. Stream-water samples were collected downstream from both the dam in zone 8c and the weir in zone 9, a detail that will have relevance when interpreting the modeling results presented later.

Surface-water samples were obtained at a single point in the centroid of flow by the grab-sampling technique using VOC sampling methods described in published NAWQA guidelines (Mueller and others, 1997; Shelton, 1997). Ground-water samples were obtained using a 1-in. diameter drive point installed in the center of the streambed channel to a depth of approximately 1 m below the streambed. The drive point was purged during installation three to four times to remove foreign matter and allowed to stabilize for approximately 8 hours prior to sampling. The drive point was purged of three volumes of water and then sampled using a peristaltic pump and clean Teflon tubing. Sampling positions were determined using a global positioning



**Figure 6.** Study section of Aberjona River (Winchester, Massachusetts) showing locations of the 10 stream zones and the confluence with Horn Pond Brook.

**Table 1.** Synoptic data for Aberjona River system, July 11–13, 2001.[km, kilometers; m, meters; m<sup>3</sup>/s, cubic meter per second; NA, not available]

Zone (see fig. 6)	Upstream zone boundary (km)	Downstream zone boundary (km)	Average stream width ( <i>w</i> ) (m)	Average stream depth ( <i>h</i> ) (m)	Streamflow at upstream end of zone ( <i>Q</i> ) (m <sup>3</sup> /s)	Change in stream- flow due to ground water ( $\Delta Q$ ) (m <sup>3</sup> /s)
Aberjona River						
1	0	0.096	5.5	0.30	0.354	0.0368
2	.096	.400	7.3	.53	.3908	.0227
3	.400	.540	7.9	.76	.4135	.0925
4	.540	1.090	22.8	.34	.5060	-.173
5	1.090	1.150	8.5	.64	.3330	.0538
6	1.150	1.230	7.3	.79	.3868	-.0595
7	1.230	1.647	3.6	.37	.3273	-.0264
8a	1.647	1.897	100.0	2.0	.3009	.0156
8b	1.897	2.147	10.0	2.0	.5185	0
8c	2.147	2.293	90.0	2.0	.5185	.0118
9	2.293	2.736	10.7	1.07	.5303	.0311
10	2.736	2.811	7.9	.64	.5614	.0510
Horn Pond Brook	1.647	1.647	NA	NA	.202	NA

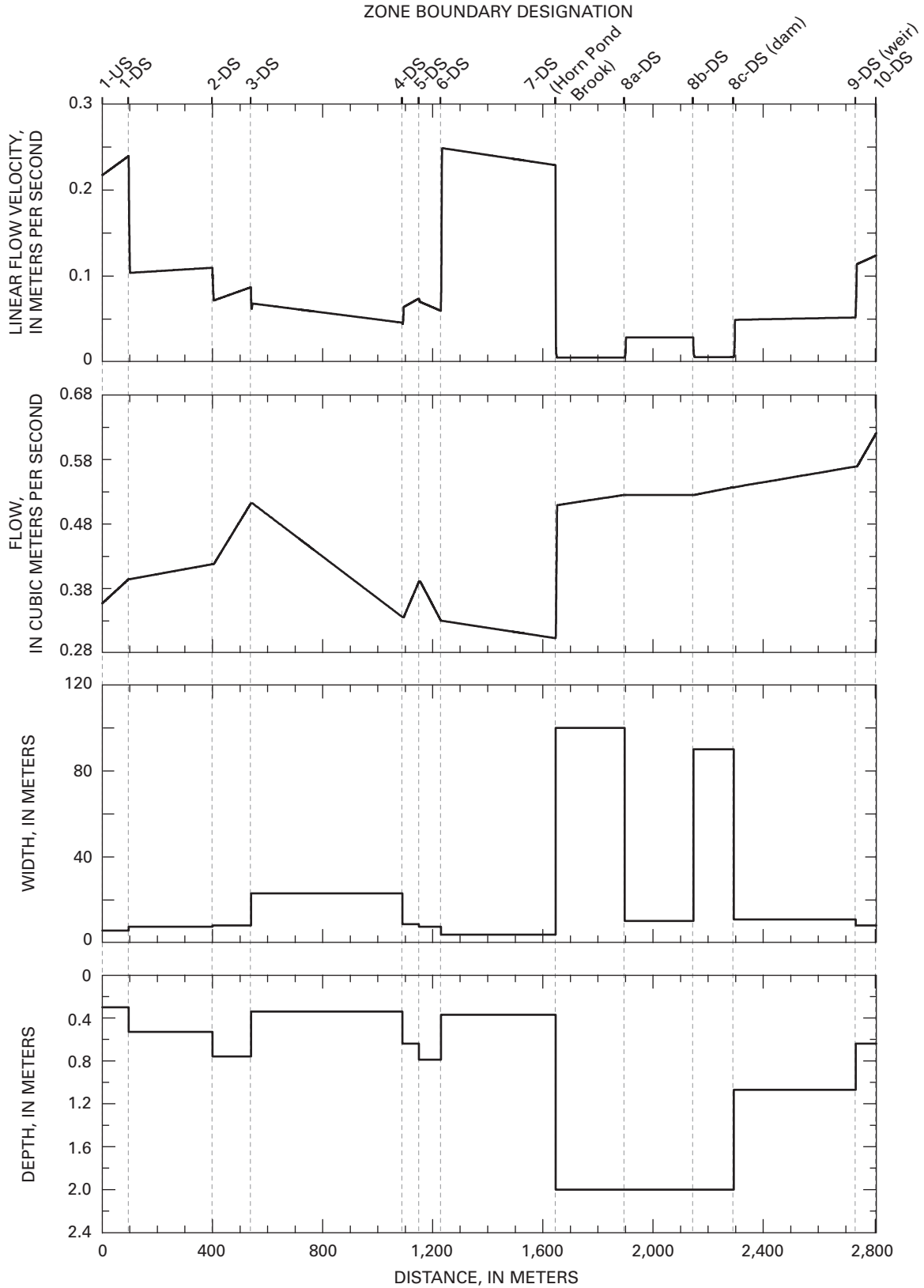
system (GPS) device. Surface-water and ground-water drive-point sample collection occurred at the 12 locations defining the upstream boundary of zone 1 and the downstream boundaries of zones 1, 2, 3, 4, 5, 6, 7, 8b, 8c, 9, and 10 shown in figure 6. Surface-water samples also were collected from the main tributary, Horn Pond Brook, at a point immediately upstream from its confluence with the river. Water concentrations of 87 VOCs were determined at the Oregon Health and Science University, Department of Biomolecular Systems Laboratory, using a method previously published by Connor and others (1998). The 87 VOCs also were determined from 10-hour composite air samples obtained at the centroid of the source-synoptic study area; the air analytical method utilized is described in detail by Pankow and others (1998).

Out of 87 total VOCs sampled, 8 compounds listed in tables 2–4 (acetone, benzene, MTBE, chloroform, 1,1-dichloroethane (1,1-DCA), *cis*-1,2-dichloroethene (*cis*-1,2-DCE), trichloroethene (TCE), and perchloroethene (PCE, also known as tetrachloroethene)) were found with sufficient spatial coverage in the Aberjona River system to allow meaningful comparison of the measured data with model results produced by StreamVOC. The method detection limit (MDL) values for the eight compounds were as follows: acetone = 0.67 µg/L; benzene = 0.014 µg/L; MTBE = 0.025 µg/L; chloroform = 0.017 µg/L; 1,1-DCA = 0.011 µg/L; *cis*-1,2-DCE = 0.013 µg/L; TCE = 0.020 µg/L; and PCE = 0.027 µg/L. In general, the MDLs are higher than the typical instrumental detection limits. Because of this, it is possible for the analysis to show that a VOC is qualitatively present in a sample even though its concentration is below the MDL. In those cases, the VOC

concentration was estimated by assuming a linear response and extrapolated using the lowest available standard for that day. In tables 2–4, an entry of ND denotes that the VOC was not qualitatively present in the sample, indicating that the concentration either was below the instrumental detection limit or was in fact zero. No attempt was made to distinguish between these two cases, and we have arbitrarily assumed a zero value for the concentration of any VOC that was listed as ND.

Replicate surface-water samples collected at the downstream end of zone 5 showed the following percent differences between the two concentrations: acetone, 58 percent; benzene, not detected (ND); MTBE, 11 percent; chloroform, 8.3 percent; 1,1-DCA, 15 percent; *cis*-1,2-DCE, 4.0 percent; TCE, 0 percent; and PCE, 27 percent (table 2). Replicate ground-water samples were collected at the downstream end of zone 1 and the downstream end of zone 10. The percent differences between these replicate samples where the VOC was detected were: acetone (zone 1), 0.6 percent; MTBE (zone 1), 6.1 percent; chloroform (zone 10), 14 percent; 1,1-DCA (zone 1), 6.2 percent; *cis*-1,2-DCE (zone 1), 16 percent; and TCE (zone 1), 12.5 percent (table 3).

The  $c_{s,i}$  values in table 4 were calculated using the measured atmospheric concentrations and  $H_i$  values obtained as follows: acetone from Zhou and Mopper (1990); benzene from Leighton and Calo (1981); chloroform, 1,1-DCA, *cis*-1,2-DCE, and PCE from Gossett (1987); MTBE from Robbins and others (1993); TCE from Ashworth and others (1988). Values of  $\bar{V}$  were based on density data found in the Beilstein Crossfire online database BS030200PR at <http://chemistry.library.wisc.edu/beilstein/home.htm>.



**Figure 7.** Physical characteristics of the Aberjona River as a function of distance where distance is measured going downstream (DS) from the upstream (US) end of zone 1 to the downstream end of zone 10 (see figure 6 for zone locations). Intervals over which flow decreases represent intervals where streamflow is being lost to ground water, and intervals over which increases represent areas where ground water is discharging to the river or where tributaries flow into the river.

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**Table 2.** Volatile organic compound (VOC) concentrations in surface-water samples obtained during a synoptic study of the Aberjona River conducted July 11–13, 2001.

[µg/L, micrograms per liter; km, kilometers; US, upstream end; DS, downstream end; HPB, Horn Pond Brook; ND, not detected. No data were collected for zone 8a]

Zone sample point	Distance (km)	Concentration (µg/L)							
		Acetone C <sub>3</sub> H <sub>6</sub> O	Benzene C <sub>6</sub> H <sub>6</sub>	Methyl <i>tert</i> -butyl ether (MTBE) C <sub>5</sub> H <sub>12</sub> O	Chloroform CHCl <sub>3</sub>	1,1-dichloroethane (1,1-DCA) C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	<i>cis</i> -1,2-Dichloroethene ( <i>cis</i> -1,2-DCE) C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	Trichloroethene (TCE) C <sub>2</sub> HCl <sub>3</sub>	Perchloroethene (PCE) C <sub>2</sub> Cl <sub>4</sub>
1-US	0	0.56	0.009	0.61	0.12	0.038	0.3	0.17	0.039
1-DS	.096	.44	ND	.63	.12	.034	.26	.18	.048
2-DS	.400	.12	ND	.58	.12	.043	.23	.16	.1
3-DS	.540	.45	ND	.58	.12	.037	.26	.15	.1
4-DS	1.090	.4	ND	.4	.1	.091	.23	.21	.14
5-DS-A <sup>1</sup>	1.150	.38	ND	.54	.12	.096	.25	.32	.15
5-DS-B <sup>2</sup>	1.150	.6	ND	.48	.11	.11	.26	.32	.19
6-DS	1.230	.58	.007	.34	.092	.095	.23	.31	.14
HPB	1.647	ND	.05	4.12	ND	ND	.032	.035	ND
7-DS	1.647	.43	ND	.54	.1	.086	.23	.32	.13
8b-DS	2.147	.46	.019	.99	.07	.062	.15	.18	.074
8c-DS	2.293	.48	.009	.8	.072	.046	.12	.18	.16
9-DS	2.736	.086	.01	1.43	.08	.051	.14	.16	.19
10-DS	2.811	.15	.012	1.36	.071	.045	.12	.16	.18

<sup>1</sup>A = first sample.

<sup>2</sup>B = second (replicate) sample.

**Table 3.** Volatile organic compound (VOC) concentrations in ground-water samples obtained during a synoptic study of the Aberjona River conducted July 11–13, 2001.

[km, kilometers; µg/L, micrograms per liter; US, upstream end; DS, downstream end; ND, not detected. No data were collected for zone 2]

Zone sample point	Distance (km)	Concentration (µg/L)							
		Acetone C <sub>3</sub> H <sub>6</sub> O	Benzene C <sub>6</sub> H <sub>6</sub>	Methyl <i>tert</i> -butyl ether (MTBE) C <sub>5</sub> H <sub>12</sub> O	Chloroform CHCl <sub>3</sub>	1,1-Dichloroethane (1,1-DCA) C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	<i>cis</i> -1,2-Dichloroethene ( <i>cis</i> -1,2-DCE) C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	Trichloroethene (TCE) C <sub>2</sub> HCl <sub>3</sub>	Perchloroethene (PCE) C <sub>2</sub> Cl <sub>4</sub>
1-US	0	0.15	ND	1.05	ND	ND	0.30	0.15	ND
1-DS-A <sup>1</sup>	.096	1.80	ND	.33	ND	0.48	.25	.24	ND
1-DS-B <sup>2</sup>	.096	1.79	ND	.35	ND	.51	.21	.21	ND
3-DS	.540	ND	ND	ND	1.16	ND	ND	.39	0.82
4-DS	1.090	.29	ND	ND	ND	ND	ND	.15	ND
5-DS	1.150	.43	ND	ND	ND	.12	.12	1.09	ND
6-DS	1.230	1.51	ND	3.17	ND	18.27	8.41	1.41	ND
7-DS	1.647	.44	ND	ND	ND	.29	.24	1.42	ND
8c-DS	2.293	.99	ND	ND	ND	ND	ND	ND	ND
9-DS	2.736	.61	ND	1.36	ND	ND	.33	ND	ND
10-DS-A <sup>1</sup>	2.811	ND	ND	ND	.35	ND	ND	ND	ND
10-DS-B <sup>2</sup>	2.811	ND	ND	ND	.40	ND	ND	ND	ND

<sup>1</sup>A = first sample.

<sup>2</sup>B = second (replicate) sample.



**Table 4.** Volatile organic compound (VOC) levels in air, water in equilibrium with that air, and in local stream water obtained during a synoptic study of the Aberjona River conducted July 11–13, 2001.

[km, kilometers; ppbv, parts per billion by volume; µg/L, micrograms per liter; MP, midpoint of zone; US, upstream end; DS, downstream end; ND, not detected]

Zone sample point	Distance (km)	Concentration							
		Acetone C <sub>3</sub> H <sub>6</sub> O	Benzene C <sub>6</sub> H <sub>6</sub>	Methyl <i>tert</i> - butyl ether (MTBE) C <sub>5</sub> H <sub>12</sub> O	Chloroform CHCl <sub>3</sub>	1,1-Dichloro ethane (1,1-DCA) C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	<i>cis</i> -1,2-Dichloro- ethene ( <i>cis</i> -1,2-DCE) C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	Trichloro- ethene (TCE) C <sub>2</sub> HCl <sub>3</sub>	Perchloro- ethene (PCE) C <sub>2</sub> Cl <sub>4</sub>
Measured air levels (ppbv)									
7-MP	1.44	0.69	0.20	0.26	0.045	ND	ND	0.014	0.073
Calculated equilibrium (Henry's Gas Law) stream-water concentrations (µg/L)									
7-MP	1.44	0.91	0.0032	0.044	0.0017	0	0	0.00020	0.00081
Measured stream-water concentrations (µg/L)									
7-US	1.23	0.58	0.007	0.34	0.092	0.095	0.23	0.31	0.14
7-DS	1.65	.43	ND	.54	.10	.086	.23	.32	.13
Stream status in zone 7—ingassing or outgassing									
7-US		ingassing <sup>1</sup>	outgassing <sup>2</sup>	outgassing	outgassing	outgassing	outgassing	outgassing	outgassing
7-DS		ingassing	undetermined <sup>3</sup>	outgassing	outgassing	outgassing	outgassing	outgassing	outgassing

<sup>1</sup>Ingassing = ingassing because the measured stream-water concentration is lower than the calculated equilibrium water concentration.<sup>2</sup>Outgassing = outgassing because the measured stream-water concentration is higher than the calculated equilibrium water concentration.<sup>3</sup>Undetermined = undetermined because the calculated equilibrium concentration is lower than the water method detection limit used to measure the stream-water concentration.

Over the entire Aberjona River synoptic study region, only acetone was undersaturated in the surface water with respect to its Henry's Gas Law equilibrium concentration. The other seven compounds were present at water concentrations that were supersaturated relative to the levels specified by equilibrium with the atmospheric levels measured in the vicinity of zone 6. In other words, the various  $c_i$  values from zones 1 through 10 for these seven VOCs were larger than the corresponding values of  $c_{s,i}$  calculated based on the  $f_i$  values. It was therefore concluded that: (1) the river was probably losing all seven compounds by volatilization over the entire study interval; and (2) for the water flowing into zone 1, the local atmosphere probably was not the origin of the majority of any of the initial seven  $c_i$  values. Because the origins of the contaminants in the flow entering zone 1 are not known, for any stream point  $(x,t)$ , the fraction of  $c_i$  due to the flow that entered zone 1 was arbitrarily assigned in this study to  $\alpha_{\text{INFLOW}}$ .

In similarity with the other seven VOCs, the mass of acetone entering zone 1 was assigned to  $\alpha_{\text{INFLOW}}$ . In contrast with a VOC where the surface water is supersaturated with respect to Henry's Gas Law, an unknown fraction of  $\alpha_{\text{INFLOW}}$  for acetone

should more correctly be assigned to the atmospheric source fraction,  $\alpha_{\text{AIR}}$ . However, without detailed information concerning the sources and surface-water concentrations of acetone upstream from zone 1, determining the fraction of  $\alpha_{\text{INFLOW}}$  that should be assigned to the atmospheric source was not possible. Therefore,  $\alpha_{\text{INFLOW}}$  for acetone was not partitioned into atmospheric and other source fractions.

The synoptic data were used with StreamVOC in model runs for the eight VOCs as follows. For each VOC, the model was initialized using the concentration measured in the stream-flow entering zone 1. After assuming that the regional air was sufficiently well mixed to allow the values of  $f_i$  and  $c_{s,i}$  obtained for zone 6 to be applicable from zones 1 through 10, gas transfer across the stream/air interface was calculated to occur according to the previous equations. Modeled sources to the stream included calculated inflows to the stream from ground water, the point source from Horn Pond Brook, and the atmosphere in the case of acetone. Modeled losses included calculated outflows from the stream to ground water and outflow to the atmosphere in the case of benzene, MTBE, chloroform, 1,1-DCA, *cis*-1,2-DCE, TCE, and PCE.

**Table 5.** Chemical degradation half-lives ( $\tau_{0.5}$ ).

[N.S., not significant based on relevant rates]

Compound	$\tau_{0.5}$ <sup>-</sup> Hydrolysis (years)	$\tau_{0.5}$ <sup>-</sup> Photolysis (years)	$\tau_{0.5}$ <sup>-</sup> Oxidation (years)
acetone	N.S. <sup>1</sup>	N.S. <sup>1</sup>	N.S. <sup>1</sup>
benzene	N.S. <sup>2</sup>	N.S. <sup>2</sup>	<sup>2</sup> 0.92
methyl <i>tert</i> -butyl ether	N.S. <sup>1</sup>	N.S. <sup>1</sup>	N.S. <sup>1</sup>
chloroform	<sup>2</sup> 1,800	N.S. <sup>2</sup>	<sup>2</sup> 78
1,1-dichloroethane	<sup>2</sup> 58	N.S. <sup>2</sup>	<sup>2</sup> 100,000
<i>cis</i> -1,2-dichloroethene	<sup>2</sup> 2.1x10 <sup>10</sup>	N.S. <sup>1</sup>	N.S. <sup>1</sup>
trichloroethene	<sup>2</sup> 1.66x10 <sup>5</sup>	N.S. <sup>2</sup>	<sup>2</sup> 10,000
perchloroethene	<sup>2</sup> 9.56x10 <sup>8</sup>	N.S. <sup>2</sup>	<sup>2</sup> 10,000

<sup>1</sup>U.S. Agency for Toxic Substances and Disease Registry, Toxicological Profile Sheet, <http://www.atsdr.cdc.gov/toxpro2.html>.

<sup>2</sup>Rathbun (2000).

Considerations of inflow and outflow from ground water in each zone made use of three assumptions: (1) inflow/outflow could be determined based on the difference in  $Q$  values measured at the zone endpoints; (2) inflow/outflow could be distributed uniformly over a given zone; and (3) when an inflow contained a VOC, the inflow concentration over the zone could be taken as being constant and equal to the value measured at the end of the zone by drive-point sampling. Compared to assigning the average zone inflow VOC concentrations to the ground-water concentration measured for that start point of that zone or assigning the average zone inflow VOC concentrations to the mean of the start point and endpoint ground-water concentrations, assigning the average zone inflow concentration as described in the third assumption gave the best overall fit between the model-simulated and measured surface-water VOC concentrations. Using zone 3 as an example of the implementation of the first assumption,  $Q$  was 0.414 m<sup>3</sup>/s at the upstream end and 0.506 m<sup>3</sup>/s at the downstream end. With no tributaries in this zone, the total inflow of ground water over zone 3 was 0.092 m<sup>3</sup>/s. Using the data in table 3, the VOC concentrations in the ground-water inflows to zone 3 are acetone = 0.0 µg/L, benzene = 0.0 µg/L, MTBE = 0.0 µg/L, chloroform = 1.16 µg/L, 1,1-DCA = 0.0 µg/L, *cis*-1,2-DCE = 0.0 µg/L, TCE = 0.39 µg/L, and PCE = 0.82 µg/L.

Typical chemical degradation half-lives,  $\tau_{0.5,i}$ , for the eight VOCs considered for this model test are listed in table 5 for hydrolysis, photolysis, and oxidation in aqueous media. The half-life for each compound is defined in terms of its first-order rate constant,  $k_{deg,i}$ , where in the absence of volatilization, dilution, or other loss processes, the concentration of the VOC as a function of time is equal to

$$c_i = c_{i,0} e^{-k_{deg,i} t}, \quad (47)$$

where  $c_{i,0}$  is the concentration of  $i$  at  $t = 0$ . Therefore,  $\tau_{0.5,i}$  is defined as  $0.693/k_{deg,i}$ . Typically, the values for  $\tau_{0.5,i}$ , when known, are on the order of years or longer. The total transit

time for a parcel of water in the source synoptic study region was approximately 52 hours. Given that this time is at least an order of magnitude smaller than the chemical degradation half-lives in table 5, chemical degradation is not likely to be important for these compounds.

Appendixes 2–1 through 2–8 list StreamVOC parameter files for the eight VOCs used in this study. The VOC sources were deduced from the synoptic study VOC concentration measurements. Appendix 3 gives the source synoptic input and output data for the eight VOCs used in this study, and Appendix 4 gives the physical and chemical properties.

## Modeling Results

### General

Figures 8–15 provide plots of the measured VOC concentrations obtained for the Aberjona River during the July 11–13, 2001, synoptic sampling. Also plotted are StreamVOC model results that simulate stream concentrations and corresponding SA fractions calculated using the net flux method based on (1) inputs determined from the synoptic-sampling effort; and (2) modified inputs derived from minimizing the reduced chi-square between the model-simulated and measured surface-water concentrations. In the case of (1), as described above, this means that in zones with ground-water inflow, the VOC concentration in the ground water was assigned to be equal to that measured during the source synoptic study, and the VOC concentration in Horn Pond Brook was taken to be that measured during the source synoptic study. In the case of (2), the ground-water inflow VOC concentrations and the VOC concentration in Horn Pond Brook were adjusted to minimize the reduced chi-square value between the model output and measured surface-water VOC concentrations. The reduced chi-square is defined as

$$\chi_i^2 = \sum_{k=1}^{N_{C,i}} \frac{(c_{i,k}^{ss} - c_{i,k}^{mod})^2}{(c_{i,k}^{ss})^2}, \quad (48)$$

where  $\chi_i^2$  is the reduced chi-square optimization parameter for VOC  $i$ ;  $N_{C,i}$  is the number of non-zero surface-water concentrations measured during the source-synoptic study;  $c_{i,k}^{ss}$  is the measured concentration of VOC  $i$  in zone  $k$ ; and  $c_{i,k}^{mod}$  is the model-simulated concentration of VOC  $i$  in zone  $k$ . Optimization of  $\chi_i^2$  was performed using the Solver.DLL nonlinear optimization package (Frontline Systems, Incline Village, Nevada). Table 6 gives  $\chi_i^2$  calculated using  $c_{i,k}^{mod}$  derived from the source-synoptic inputs and the minimum value of  $\chi_i^2$  found by the optimization software. With the exception of acetone, the ratio of the initial to final  $\chi_i^2$  values shows that the optimization was highly significant statistically at the 99-percent confidence level. Table 7 lists the optimized VOC inputs that were found to minimize  $\chi_i^2$  between the measured and model-simulated surface-water VOC concentrations. StreamVOC parameter files for the eight VOCs used in this test model are shown in Appendixes 2–9 through 2–16.

**Table 6.** Reduced chi-square values calculated between the measured surface-water volatile organic compound (VOC) concentrations and concentrations estimated using the source synoptic VOC inputs and inputs optimized to minimize the reduced chi-square value,  $\chi_i^2$ .

	$\chi_i^2$							
	Acetone (ACE)	Benzene (BEN)	Methyl <i>tert</i> - butyl ether (MTBE)	Chloroform (CLF)	1,1-Dichloro- ethane (1,1-DCA)	<i>cis</i> -1,2- Dichloro- ethene ( <i>cis</i> -1,2-DCE)	Trichloro- ethene (TCE)	Perchloro- ethene (PCE)
Source synoptic inputs	69	0.42	1.6	4.9	6.4	3.5	2.4	4.3
Optimized inputs	44	.032	.19	.066	.37	.037	.12	.21
Ratio	1.6	13	8.4	74	17	92	20	21

As noted previously, for each of the eight VOCs,  $\alpha_{\text{INFLOW}}$  is the SA fraction corresponding to the portion of the VOC that entered the system at the upstream end of zone 1. Also, using the net flux method, because all of the VOCs except acetone were volatilizing over all 10 zones of the stream to the atmosphere, only the plots for acetone contain a non-zero value for the atmospheric source,  $\alpha_{\text{AIR}}$ . For the other seven compounds,  $\alpha_{\text{AIR}} = 0$  over all  $x$  and  $t$  using the net flux method. However, using the component flux method results in non-zero  $\alpha_{\text{AIR}}$  for several other VOCs in addition to acetone.

### Acetone

The synoptic sampling effort identified six sources of acetone for the Aberjona River study interval: the stream inflow to the study interval at the upstream end of zone 1 (1-US), the atmosphere, and ground water entering zones 1, 5, 8c, and 9. The concentration of acetone as a function of distance in the study region calculated by StreamVOC using the acetone inputs derived directly from the source synoptic data is shown in figure 8A as the solid line. The SA calculations for the acetone inputs as determined directly from the data are shown in figure 8B.

The dashed line shown in figure 8A represents the StreamVOC results from the model where the acetone concentrations in the ground water and Horn Pond Brook sources were adjusted to give the minimum value of  $\chi^2$  defined in equation 48 (table 7). In the case of acetone, this process determined that the best fit was obtained by setting all sources in the study region except the atmospheric source to zero. Figure 8C shows the SA calculations using the net flux method for the modified inputs, where only the initial source of acetone entering zone 1 and the atmospheric source are used.

As mentioned previously, acetone is the only VOC used in the study where  $c_{s,\text{acetone}} > c_{\text{acetone}}$ , implying that there is a net flux of acetone from the atmosphere into the stream water. The effect of this flux on the SA calculations is clearly seen in figure 8B and 8C as the atmospheric source fraction,  $\alpha_{\text{air}}$ , increases in both cases from zero at the upstream end of zone 1 to approximately 45 percent at the downstream end of zone 10 for the source synoptic inputs in figure 8B and 65 percent for the optimized inputs in figure 8C. The effects of the dam at the downstream end of zone 8C and the weir at the downstream end

of zone 9 on acetone are seen as a step increase in  $\alpha_{\text{ACE,AIR}}$  at both locations. In comparison to the other seven VOCs modeled and described in the following sections, the two structures have relatively little effect on acetone because it has the highest solubility and, therefore, lowest transfer efficiency,  $E_{\text{ACE}}(H_{\text{ACE}})$ .

Figure 8D shows the SA calculations using the component flux method for the source synoptic inputs. Because acetone is undersaturated and  $\alpha_{\text{ACE,AIR}}$  is increasing even for the net flux method, the results are similar to the corresponding results in figure 8B except the final  $\alpha_{\text{ACE,AIR}}$  value is larger. For the source-synoptic inputs,  $\alpha_{\text{ACE,AIR}}$  is a little more than 75 percent at the downstream end of zone 10 using the component flux method compared with the 45 percent resulting from the net flux method.

### Benzene

The synoptic sampling effort identified two sources of benzene for the Aberjona River study interval—the stream inflow to the study interval at the upstream end of zone 1 and Horn Pond Brook. The model-simulated benzene concentrations shown in figure 9A (solid line) and the SA calculations using the net flux method in figure 9B are based on model inputs from the synoptic sampling. The decreasing benzene concentrations over zones 1 through 6 (fig. 9A) are because  $c_{\text{BEN}} > c_{s,\text{BEN}}$  throughout that range, and thus the stream loses benzene to the atmosphere. The same observation applies to the concentration trend observed over zones 8b through 10. The magnitude of the concentration increase between zone 6 and zone 8b is consistent with the increase estimated based on the benzene concentration and flow discharge of Horn Pond Brook, and there is good agreement between the measured and model-simulated concentrations in zones 6, 8b, and 8c. However, the measured and model-simulated concentrations diverge in zones 9 and 10 downstream from the two hydraulic structures.

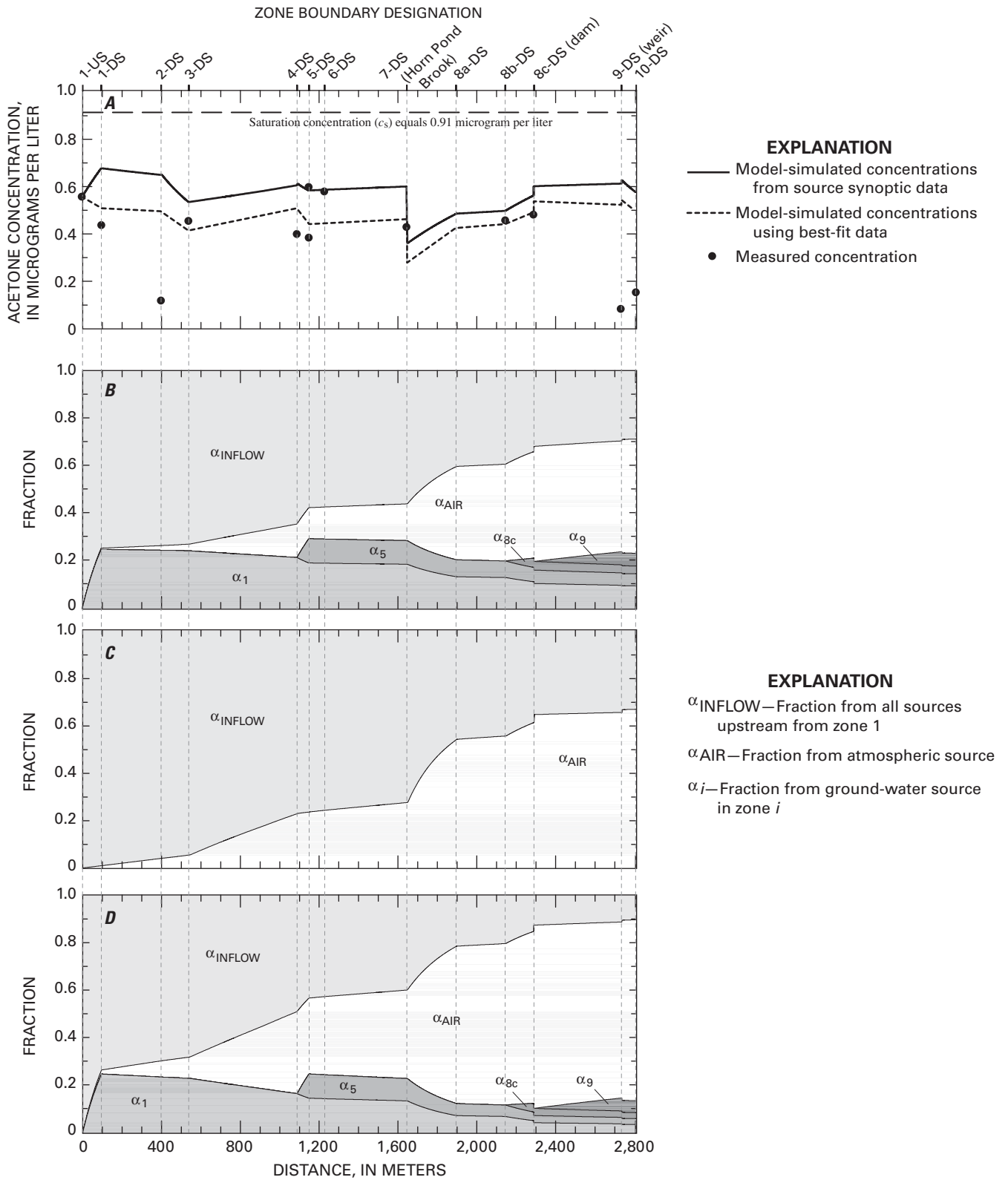
Because  $H_i$  for benzene is a factor of 100 larger than for acetone, the weir transfer efficiency is much larger for benzene. This is reflected in the large drop in benzene concentrations at each of the two structures. However, following the theoretical discussion presented in the governing equations, there is no change in the SA because the river is outgassing VOC over the structures.

**Table 7.** Volatile organic compound (VOC) concentrations in Horn Pond Brook and ground-water inflows to the Aberjona River that minimize the reduced chi-square value between the measured and StreamVOC model-simulated surface-water VOC concentrations.

[µg/L, micrograms per liter, HPB, Horn Pond Brook; NC, no change]

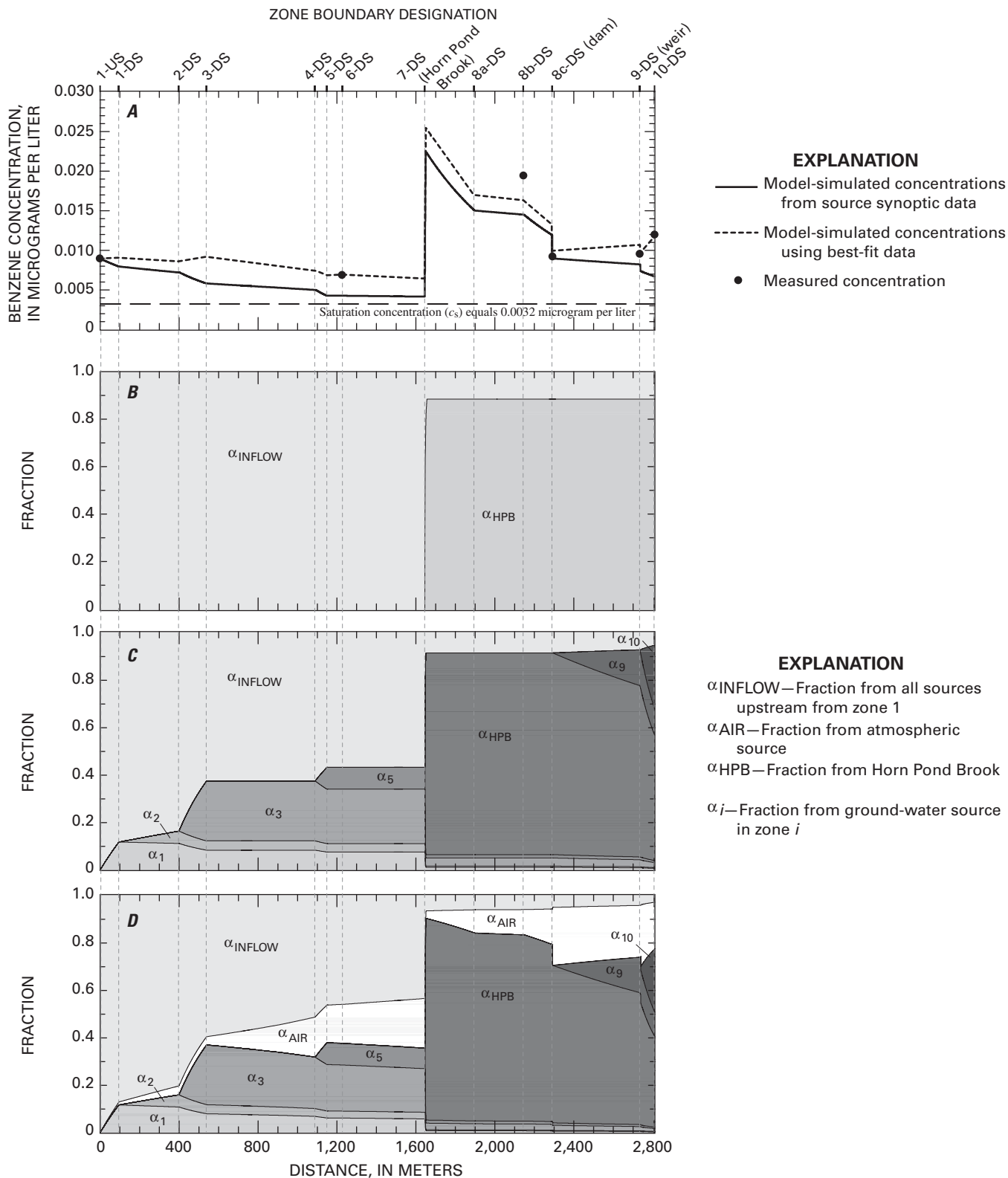
Zone	Estimated concentration and concentration difference (µg/L)															
	Acetone (ACE)		Benzene (BEN)		Methyl <i>tert</i> -butyl ether (MTBE)		Chloroform (CLF)		1,1-Dichloroethane (1,1-DCA)		<i>cis</i> -1,2-Dichloroethene ( <i>cis</i> -1,2-DCE)		Trichloroethene (TCE)		Perchloroethene (PCE)	
	Concentration <sup>1</sup>	Difference <sup>2</sup>	Concentration <sup>1</sup>	Difference <sup>2</sup>	Concentration <sup>1</sup>	Difference <sup>2</sup>	Concentration <sup>1</sup>	Difference <sup>2</sup>	Concentration <sup>1</sup>	Difference <sup>2</sup>	Concentration <sup>1</sup>	Difference <sup>2</sup>	Concentration <sup>1</sup>	Difference <sup>2</sup>	Concentration <sup>1</sup>	Difference <sup>2</sup>
1	0	-1.79	0.012	0.012	0.92	0.58	0.19	0.19	0.0033	-0.48	0	-0.23	0.25	0.043	0.14	0.14
2	0	NC	.0084	.0084	.078	.078	.20	.20	.26	.26	0	NC	.14	.14	1.08	1.08
3	0	NC	.013	.013	.47	.47	.19	-.97	.047	.047	.54	.54	.26	-.13	.21	-.61
5	0	-.43	.0046	.0046	.71	.71	.26	.26	.55	.43	.68	.56	1.65	.56	.64	.64
HPB	0	NC	.054	.004	3.23	-.89	.16	.16	.13	.13	.33	.30	.34	.30	.091	.091
8c	0	-.99	0	NC	13.4	13.4	2.82	2.82	1.15	1.15	3.59	3.59	6.45	6.45	8.78	8.78
9	0	-.61	.03	.03	16.7	15.3	.56	.56	.36	.36	1.04	.71	.65	.65	1.53	1.53
10	0	NC	.038	.038	.73	.73	0	-.37	0	NC	0	NC	.19	.19	.11	.11

<sup>1</sup>Estimated source concentration (in µg/L) used to provide best match.<sup>2</sup>Difference between source concentration used to provide best match and source concentration from the synoptic data set.



**Figure 8.** Acetone in the Aberjona River showing (A) concentrations; (B) estimated source apportionment (SA) values for sources derived from synoptic survey; (C) estimated SA values for sources chosen to provide best fit of acetone concentrations; and (D) estimated SA values calculated using the component flux method for sources determined by the source synoptic study data set. Distance is measured going downstream (DS) from the upstream (US) end of zone 1 to the downstream end of zone 10 (see figure 6 for locations).

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**Figure 9.** Benzene in the Aberjona River showing (A) concentrations; (B) estimated source apportionment (SA) values for sources derived from synoptic survey; (C) estimated SA values for sources chosen to provide best fit of benzene concentrations; and (D) estimated SA values calculated using the component flux method for sources chosen to provide best fit of benzene concentrations. Distance is measured going downstream (DS) from the upstream (US) end of zone 1 to the downstream end of zone 10 (see figure 6 for locations).

The dotted line in figure 9A shows benzene concentrations calculated by StreamVOC using modified benzene concentrations for ground-water sources and Horn Pond Brook to provide a best fit to the measured concentrations by minimizing  $\chi^2$  defined in equation 48 (see table 7). The optimization added benzene sources in zones 1, 2, 3, 5, 9, and 10 with concentrations of 0.012, 0.0084, 0.013, 0.0046, 0.030, and 0.038  $\mu\text{g/L}$ , respectively, and increased the concentration of benzene in Horn Pond Brook from 0.050 to 0.054  $\mu\text{g/L}$  (table 7). The sources in zones 9 and 10 were comparatively large to compensate for the aeration and concomitant VOC loss over the weir at the end of zone 9 and the increase in benzene measured between zones 9 and 10.

The SAs calculated by StreamVOC for the optimized sources are shown in figure 9C. Comparing the SA of the Horn Pond Brook source in figure 9B with the corresponding SA results in figure 9C shows that  $\alpha_{\text{HPB}}$  decreased from about 90 percent to approximately 50 percent between the two source input data sets.

SAs for benzene calculated using the component flux method and the optimized sources are shown in figure 9D. Comparing figure 9C with figure 9D shows the difference between the net flux method and component flux method in the case of a VOC with a surface-water concentration that is supersaturated with respect to Henry's Gas Law equilibrium yet with a relatively high atmospheric concentration (for example, benzene almost reaches Henry's Gas Law equilibrium in zones 5, 6, and 7). In the net flux method, there is no change in any of the  $\alpha$  values in the absence of sources or at the dam and weir. In contrast, in the component flux method  $\alpha_{\text{BEN,AIR}}$  increases if no other sources are influencing benzene. Furthermore, large step increases in  $\alpha_{\text{BEN,AIR}}$  are seen at the dam and weir because benzene has a relatively low Henry's Gas Law solubility and the hydraulic structures are very efficient at promoting exchange for an insoluble gas. The net effect on the SA calculations is that at the downstream end of zone 10, the component flux method results in  $\alpha_{\text{BEN,AIR}} = 20$  percent. In contrast, the net flux method yields  $\alpha_{\text{BEN,AIR}} = 0$  at the same location.

### Methyl *tert*-Butyl Ether

The synoptic sampling effort identified four sources of MTBE for the Aberjona River study interval: the stream inflow to the study interval at the upstream end of zone 1, ground-water sources entering zones 1 and 9, and Horn Pond Brook. The synoptic-based inputs lead to model-simulated MTBE concentrations (shown as the solid line in fig. 10A) that are in reasonable agreement with the measured concentration values (data points). As an example, the synoptic-based inputs simulate the existence of an increase in MTBE concentration downstream from the confluence between the Aberjona River and Horn Pond Brook, and a decrease in MTBE concentration from zone 8c to zone 9 due to the aeration of the stream at the dam. Both of these effects are seen in the model results in figure 10A. However, the measured increase of MTBE in zone 9 is not seen

in the model results using the MTBE inputs derived from the source synoptic study.

The dashed line (fig. 10A) was obtained after adjusting the MTBE sources to minimize  $\chi^2$  defined in equation 48. The optimization added sources in zones 2, 3, 5, 8c, and 10 with MTBE values of 0.078, 0.47, 0.71, 13.4, and 0.73  $\mu\text{g/L}$ , respectively, increased MTBE for the sources already present in zones 1 and 9 to 0.92 and 16.7  $\mu\text{g/L}$ , respectively, and decreased MTBE in Horn Pond Brook by approximately 20 percent to 3.23  $\mu\text{g/L}$  (table 7). Using the modified sources, MTBE concentrations simulated by StreamVOC are in excellent agreement with MTBE concentrations measured during the source synoptic study. Interestingly, nearly the same modifications required for MTBE also were required in the case of benzene. In particular, it was necessary to add relatively large sources for both MTBE and benzene in zone 5 and zone 9.

SA results corresponding to the synoptic-based inputs are given in figure 10B; SA results corresponding to the modified inputs are given in figure 10C. For the synoptic-based simulation, approximately 86 percent of the MTBE in the water is from Horn Pond Brook at the end of zone 10 (fig. 10B). In contrast, for the optimized sources, only 34 percent of the MTBE is from Horn Pond Brook (fig. 10C), with the difference in  $\alpha_{\text{MTBE,HPB}}$  between the two cases due mainly to the effect of the source in zone 9 for the optimized case.

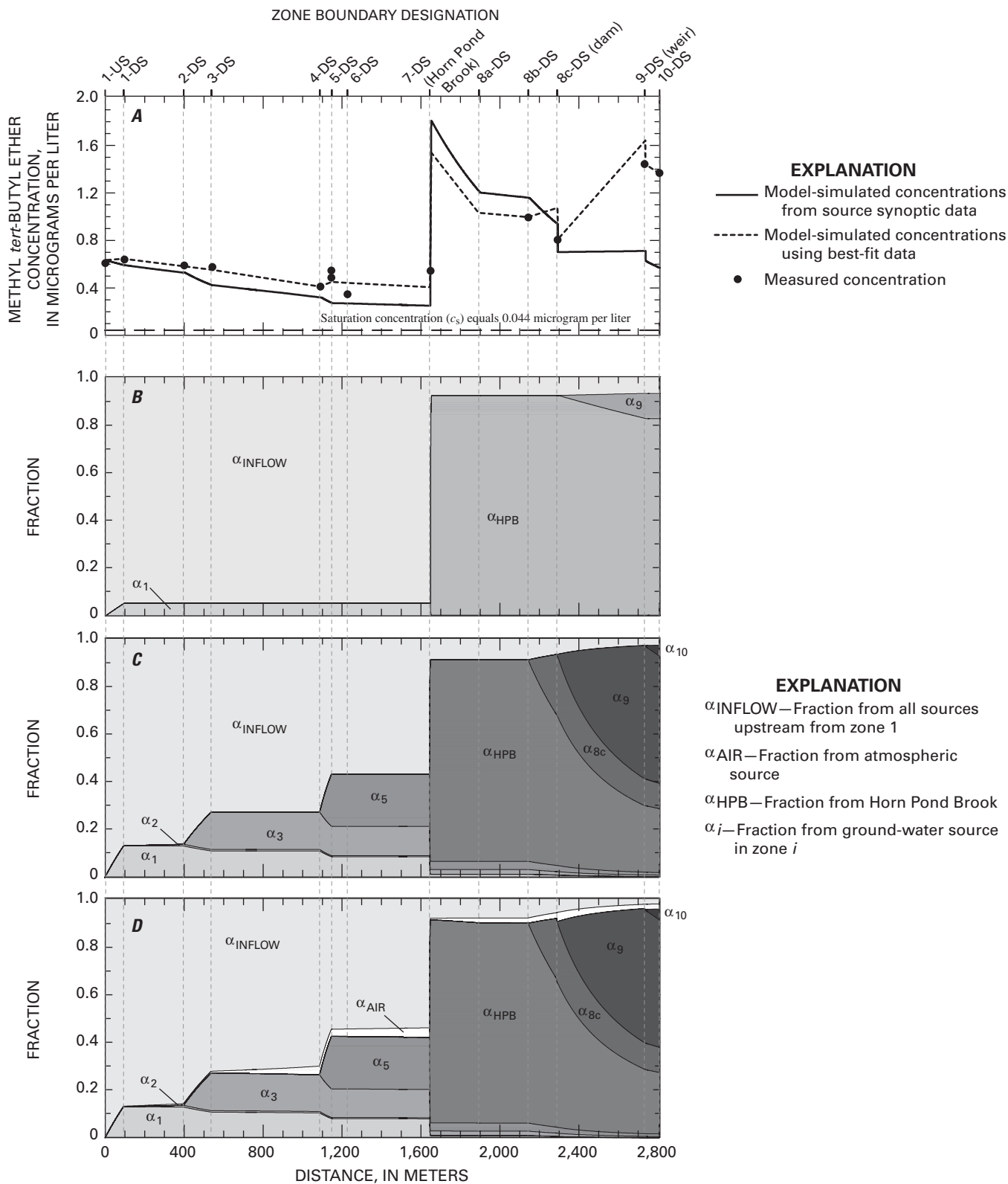
The SA results for MTBE using the optimized sources and the component flux method are shown in figure 10D. Although  $\alpha_{\text{MTBE,AIR}}$  is greater than zero, there is little difference between the net flux method and component flux method for MTBE. This is because the MTBE concentration is substantially greater than Henry's Gas Law equilibrium over much of the source synoptic study region and its relatively high solubility decreases the effectiveness of the hydraulic structures on the exchange of MTBE between water and air.

### Chloroform

The synoptic sampling effort identified three sources of chloroform for the Aberjona River study interval: the stream inflow to the study interval at the upstream end of zone 1 and ground water entering zones 3 and 10.

The model-simulated concentrations (solid line in fig. 11A) based on the inputs from the synoptic sampling, however, do not lead to a good match with the measured concentrations. In particular, the synoptic-based inputs result in a concentration peak extending over zones 3 through 7 that is not observed in the measured concentrations. One possible reason is that the ground-water concentration of 1.16  $\mu\text{g/L}$  greatly overestimates the true average chloroform concentration in the zone 3 ground-water source.

The dotted line in figure 11A shows model-simulated chloroform concentrations using modified concentrations for ground-water sources and Horn Pond Brook to give the best overall fit to the measured concentrations (table 7). The changes to the source concentrations that were required to minimize  $\chi^2$  were as follows: ground-water sources were added in



**Figure 10.** Methyl *tert*-butyl ether (MTBE) in the Aberjona River showing (A) concentrations; (B) estimated source apportionment (SA) values for sources derived from synoptic survey; (C) estimated SA values for sources chosen to provide best fit of MTBE concentrations; and (D) estimated SA values calculated using the component flux method for sources chosen to provide best fit of MTBE concentrations. Distance is measured going downstream (DS) from the upstream (US) end of zone 1 to the downstream end of zone 10 (see figure 6 for locations).



zones 1, 2, 5, 8c, and 9 with concentrations of 0.19, 0.20, 0.26, 2.82, and 0.56  $\mu\text{g/L}$ , respectively; a chloroform source from Horn Pond Brook was added by increasing chloroform in Horn Pond Brook from 0 to 0.16  $\mu\text{g/L}$ ; the chloroform was decreased for the source in zone 3 from 1.16 to 0.19  $\mu\text{g/L}$ ; and the source in zone 10 was eliminated. The corresponding modified SA results for these new inputs are given in figure 11C. The SA calculations for the synoptic data set shown in figure 11B show that 25 percent of the chloroform at the end of the study region came from the ground-water source in zone 3, with 65 percent coming from the source in zone 10. In contrast, the SA calculations for the modified sources show that less than 5 percent of the chloroform in the water at the end of zone 10 is from zone 3, with the largest source fractions now due to sources in zones 8c and 9.

The solubility of chloroform is similar to that of benzene; therefore, chloroform and benzene are affected in a similar manner by the dam spillway and weir at the ends of zones 8c and 9, respectively. Relatively large sources are required in zones 8c and 9 to balance the simulated loss in VOC concentrations by aeration at the structures. As described in the following sections, this is a common feature of the model results for the chlorinated VOCs modeled in this study, all of which were outgassing from the stream.

The SA results for the component flux method using the optimized source inputs are shown in figure 11D. The atmospheric concentration of chloroform is small so that the stream is outgassing and never close to equilibrium in the synoptic study region. Therefore,  $\alpha_{\text{CLF,AIR}}$  is only a few percent at the downstream end of zone 10.

### 1,1-Dichloroethane

The synoptic sampling effort identified three sources of 1,1-DCA for the Aberjona River study interval: the stream inflow to the study interval at the upstream end of zone 1 and ground water entering both zones 1 and 5. The inputs from the synoptic sampling lead to model results (solid line in fig. 12A) that qualitatively capture some of the changes observed in the measured concentrations. For example, the concentration increase occurring within zones 4 and 5, the decrease that occurs over zone 3 due to the VOC flux to the atmosphere and dilution from ground-water inflow, and the decrease that occurs in zone 8a because of dilution from Horn Pond Brook. The synoptic-based inputs, however, do not lead to a good quantitative match between the model-simulated results and the measured concentration data. In particular, the input from ground water over zone 1 leads to an overestimation of 1,1-DCA concentrations from zones 2 to 4, and the input from ground water over zone 5 leads to an underestimation of the concentrations from zones 5 to 10. The SA calculations for the synoptic study sources shown in figure 12B indicate that at the end of zone 10, the three synoptic study-based sources each have an SA fraction of approximately one-third.

The dotted line in figure 12A shows model-simulated concentrations obtained after modifying the model input ground-water concentrations to minimize  $\chi^2$  defined in equation 48. The results were that the 1,1-DCA ground-water concentration was reduced in zone 1 from 0.48 to 0.0033  $\mu\text{g/L}$ , the concentration was increased in zone 5 from 0.12 to 0.55  $\mu\text{g/L}$ , ground-water 1,1-DCA sources were added in zones 2, 3, 8c, and 9 with concentrations of 0.26, 0.047, 1.15, and 0.36  $\mu\text{g/L}$ , respectively, and the concentration in Horn Pond Brook was increased from 0 to 0.13  $\mu\text{g/L}$  (table 7). Corresponding SA results for the modified sources are given in figure 12C and indicate that there is no dominant source of 1,1-DCA in the water at the end of zone 10. Similar to benzene, chloroform, and MTBE, relatively large sources were required in zones 8c and 9 to offset the loss of 1,1-DCA through aeration at the dam and weir. Because the atmospheric concentration of 1,1-DCA was zero, there is no difference between the net flux method and component flux method.

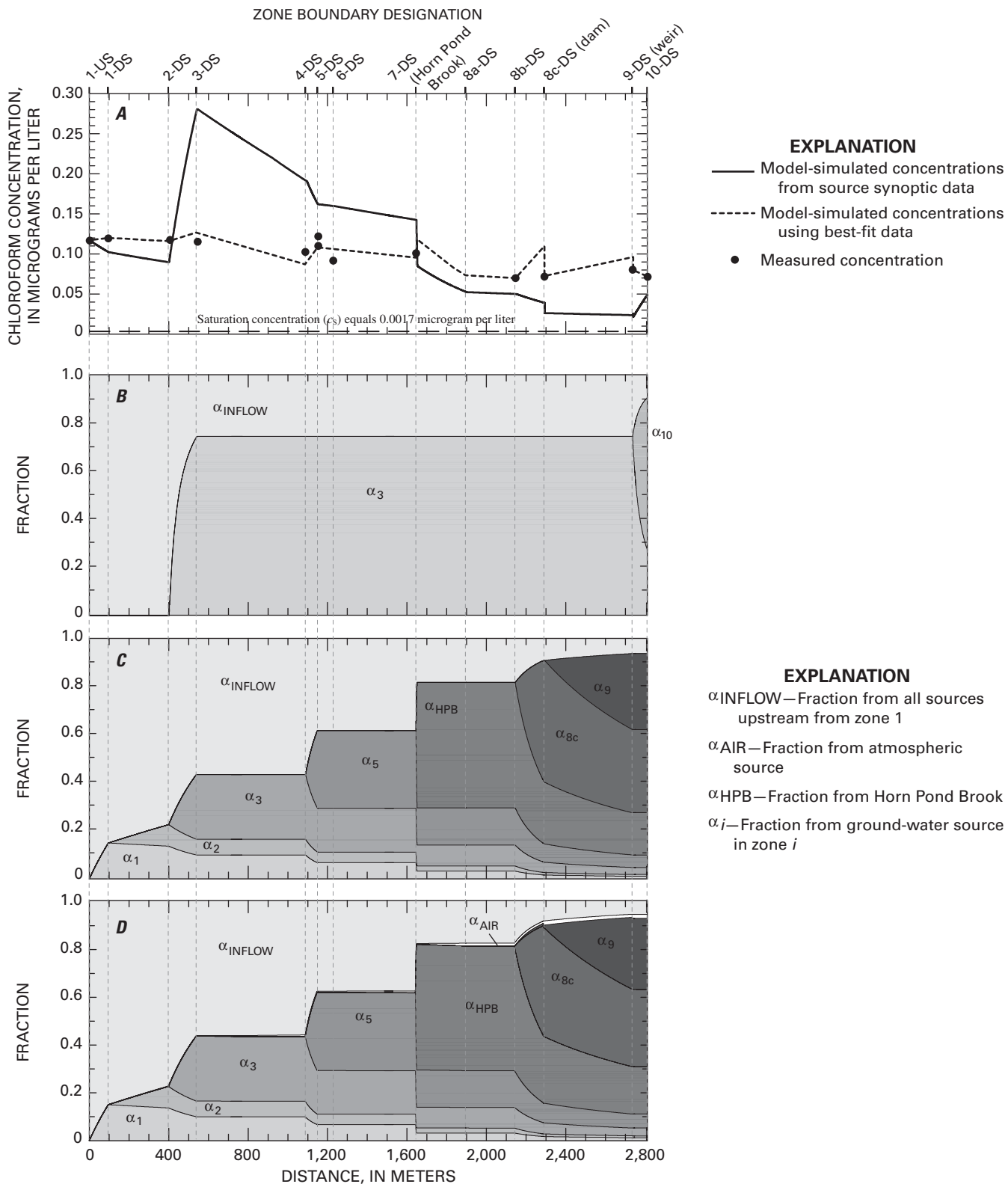
### *cis*-1,2-Dichloroethene

The synoptic sampling effort identified five sources of *cis*-1,2-DCE for the Aberjona River study interval: the stream inflow to the study interval at the upstream end of zone 1, ground water entering zones 1, 5, and 9, and the water entering from Horn Pond Brook. For zones 1 and 2, the synoptic-based inputs lead to model-simulated concentrations (solid line in fig. 13A) that agree with the measured concentrations. Also, for zones 5 through 8c, there is a general downward concentration trend both in the model results and in the measured data, including the marked drop in concentration caused by the dilution from the inflow of Horn Pond Brook at the beginning of zone 8a. However, for zones 5 through 10, the model-simulated concentrations are a factor of two less than the measured concentrations.

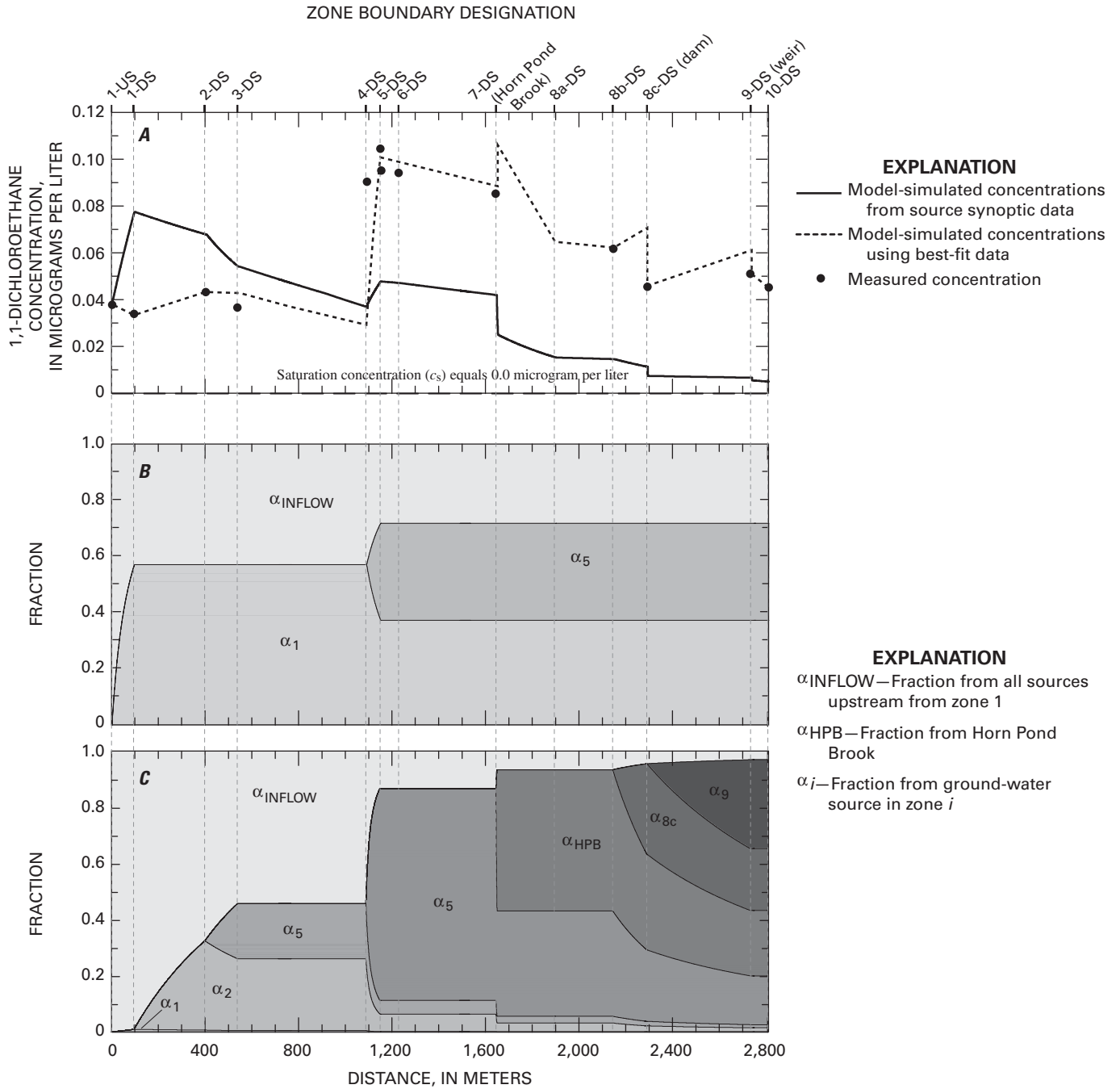
The SA calculations for the *cis*-1,2-DCE inputs identified in the synoptic study are shown in figure 13B. In this case, the two major sources of *cis*-1,2-DCE at the end of zone 10 are the source due to the water entering the study region at the beginning of zone 1 and the ground-water source in zone 9.

The dashed simulation line (fig. 13A) was obtained after optimizing the *cis*-1,2-DCE inputs by minimizing  $\chi^2$  defined in equation 48. This process resulted in the addition of *cis*-1,2-DCE sources in zones 3 and 8c with concentrations of 0.54 and 3.59  $\mu\text{g/L}$ , respectively; increasing *cis*-1,2-DCE for the sources in zones 5 and 9 and Horn Pond Brook to 0.68, 1.04, and 0.33  $\mu\text{g/L}$ , respectively; and eliminating the ground-water source of *cis*-1,2-DCE in zone 1 (see table 7). The SA results for these optimized sources are shown in figure 13C and indicate that in this case there is no dominant source of *cis*-1,2-DCE to the Aberjona River in the study region.

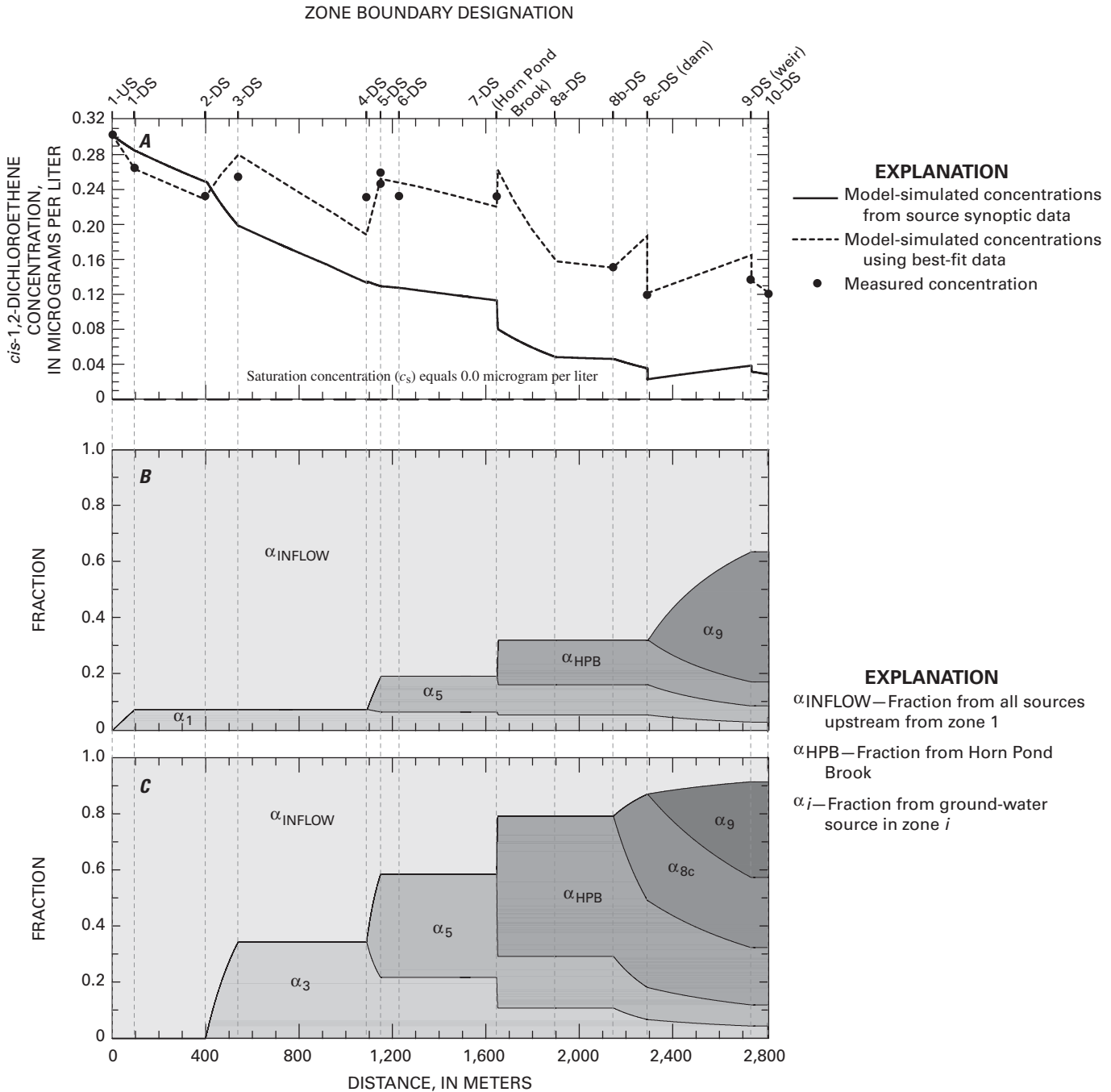
As was the case with 1,1-DCA, the atmospheric concentration of *cis*-1,2-DCE was zero. Therefore, there is no difference in the SA results between the net flux method and component flux method.



**Figure 11.** Chloroform in the Aberjona River showing (A) concentrations; (B) estimated source apportionment (SA) values for sources derived from synoptic survey; (C) estimated SA values for sources chosen to provide best fit of chloroform concentrations; and (D) estimated SA values calculated using the component flux method for sources chosen to provide best fit of chloroform concentrations. Distance is measured going downstream (DS) from the upstream (US) end of zone 1 to the downstream end of zone 10 (see figure 6 for locations).



**Figure 12.** 1,1-Dichloroethane (1,1-DCA) in the Aberjona River showing (A) concentrations; (B) estimated source apportionment (SA) values for sources derived from synoptic survey; and (C) estimated SA values for sources chosen to provide best fit for 1,1-DCA concentrations. Distance is measured going downstream (DS) from the upstream (US) end of zone 1 to the downstream end of zone 10 (see figure 6 for locations).



**Figure 13.** *cis*-1,2-Dichloroethene (*cis*-1,2-DCE) in the Aberjona River showing (A) concentrations; (B) estimated source apportionment (SA) values for sources derived from synoptic survey; and (C) estimated SA values for sources chosen to provide best fit of *cis*-1,2-DCE concentrations. Distance is measured going downstream (DS) from the upstream (US) end of zone 1 to the downstream end of zone 10 (see figure 6 for locations).

### Trichloroethene

The synoptic sampling effort identified five sources of TCE for the Aberjona River study interval: the stream inflow to the study interval at the upstream end of zone 1, ground water entering zones 1, 3, and 5, and the tributary flow from Horn Pond Brook. The synoptic-based inputs lead to model results (solid line in fig. 14A) that qualitatively capture the changes observed in the measured concentrations but underestimate the measured concentrations from zones 5 through 10. SA results corresponding to the synoptic-based simulation are given in figure 14B.

The dashed simulation line (fig. 14A) was obtained by optimizing the TCE sources to minimize  $\chi^2$  for TCE defined in equation 48. The optimization found the minimum  $\chi^2$  was obtained by decreasing TCE for the source in zone 3 from 0.39 to 0.26  $\mu\text{g/L}$ , adding VOC sources in zones 2, 8c, 9, and 10 with concentrations of 0.14, 6.45, 0.65, and 0.19  $\mu\text{g/L}$ , respectively, and increasing TCE in Horn Pond Brook and the TCE source in zone 5 to 0.34 and 1.65  $\mu\text{g/L}$ , respectively (table 7). The corresponding SA results for the modified sources are given in figure 14C.

The SA results for the synoptic study sources show that the ground-water sources in zones 1, 3, and 5 account for nearly two-thirds of the TCE in the water at the end of zone 10. In contrast, the SA calculations for the modified sources indicate that only 18 percent of the TCE is due to ground-water inflow from these same zones. As observed for 1,1-DCA and *cis*-1,2-DCE, the downstream sources had a larger effect on TCE concentrations at the end of the synoptic study region than sources farther upstream. The SA results in figure 14C show that in the modified source cases, nearly one-half of the TCE in the Aberjona River at the downstream end of zone 10 is due to the sources in zones 8c, 9, and 10. In both cases, Horn Pond Brook contributes less than 10 percent of the TCE to the river at the end of the study region.

The solubility of TCE is relatively low, so there are large decreases in TCE at the end of zones 8c and 9 due to aeration by the dam and weir, respectively. This simulated decrease in TCE at these locations requires adding large TCE sources upstream from the structures to compensate for the loss of VOC. The SA calculations made using the component flux method show that because of the low atmospheric concentration of TCE,  $\alpha_{\text{TCE,AIR}} = 0.09$  percent at the downstream end of zone 10 for the optimized TCE sources.

### Perchloroethene

The synoptic sampling effort identified two sources of PCE for the Aberjona River study interval: the stream inflow to the study interval at the upstream end of zone 1 and ground water entering over zone 3. The synoptic-based inputs lead to model-simulated results (solid line in fig. 15A) that agree with the measured concentrations in that both show (1) an increase in PCE concentration over zone 1 to zone 3; and (2) a decrease in PCE concentration caused by the inflow of Horn Pond Brook

water. However, the simulated synoptic-source inputs fail to capture the increase in concentrations from zone 3 to zone 6 and from zone 8c to zone 9, and do not show any effect of the dam spillway at the downstream end of zone 8c and the weir at the downstream end of zone 9.

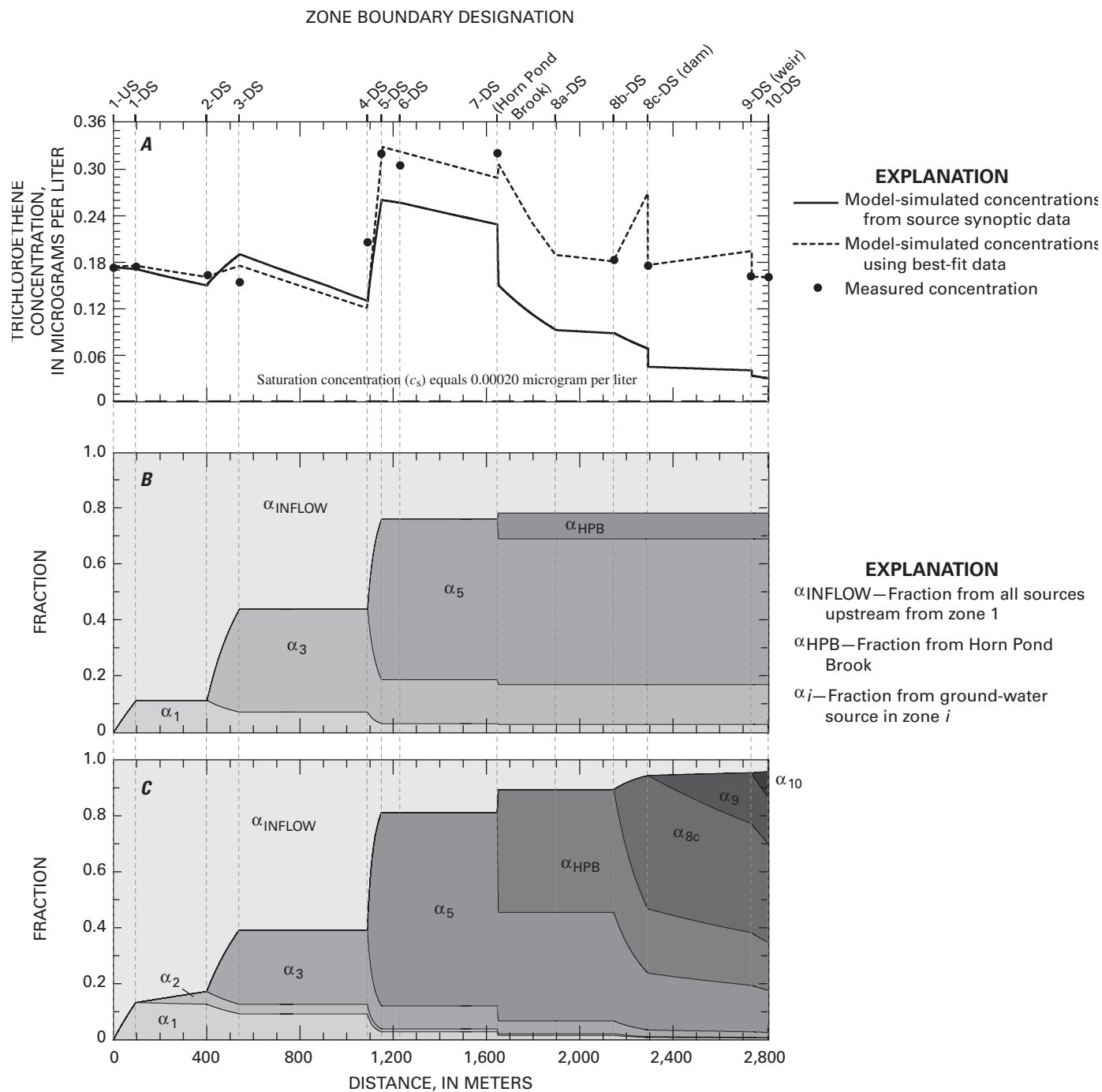
The dashed simulation line (fig. 15A) was obtained after modifying the model inputs to minimize  $\chi^2$  defined in equation 48 as shown in table 7 by decreasing PCE for the source in zone 3 from 0.82 to 0.21  $\mu\text{g/L}$ ; adding PCE sources in zones 1, 2, 5, 8c, 9, and 10 with concentrations of 0.14, 1.08, 0.64, 8.78, 1.53, and 0.11  $\mu\text{g/L}$ , respectively; and adding a source from Horn Pond Brook by increasing its PCE from 0 to 0.091  $\mu\text{g/L}$ . There is much better agreement between the measured and model-simulated concentrations for PCE.

SA results calculated using the net flux method for the sources derived from the synoptic survey are given in figure 15B. Not surprisingly, the major source of PCE to the Aberjona River over the synoptic study region is the ground-water source in zone 3. The corresponding SA results for the modified PCE sources using the net flux method are given in figure 15C. The sources in zones 8c and 9 account for approximately 80 percent of the PCE in the stream at the end of zone 10. Because of the low atmospheric concentration of PCE, there is essentially no difference between the SA results for the net flux method and the component flux method. For example, using the optimized PCE inputs,  $\alpha_{\text{PCE,AIR}} = 0.30$  percent at the downstream end of zone 10.

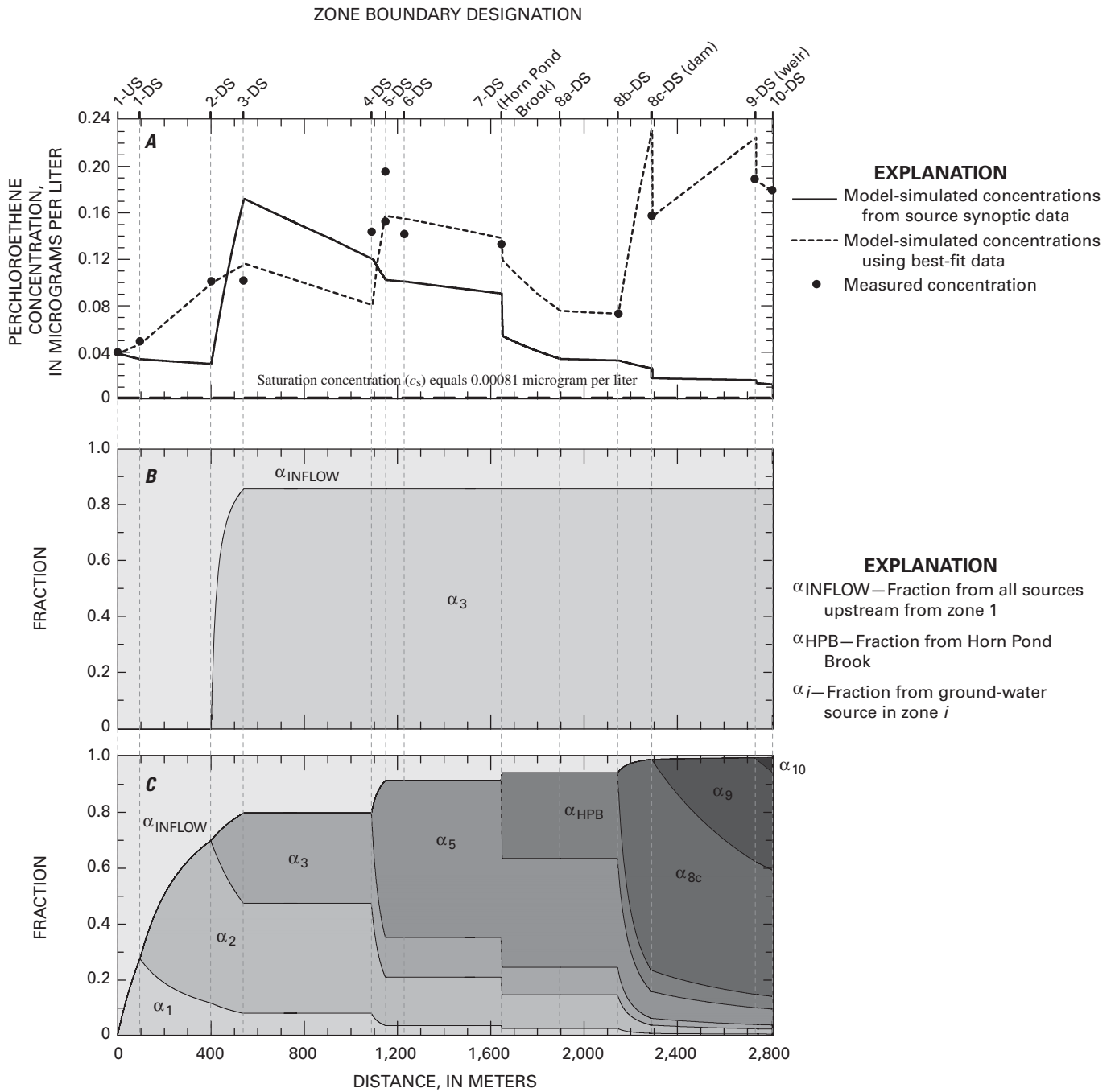
## Synopsis of StreamVOC Simulation Results

The values for  $\chi_i^2$  in table 6 show that benzene, MTBE, and TCE were the three compounds for which the synoptic-based sampling inputs led to the best general agreement between the StreamVOC-simulated concentrations and the measured concentrations and that acetone was by far the worst. It is not clear why the model fails to capture any of the major changes in the measured surface-water concentration of acetone. However, in the case of benzene and MTBE, the major source of VOC in the synoptic study region was Horn Pond Brook. Because this was a surface-water source, the concentration for each compound along with the flow volume added to the stream (and the resulting source term equal to the product of the concentration and the flow) was more easily characterized in terms of the total mass input to the Aberjona River. Therefore, it is not surprising that the accuracy of the model in terms of reproducing the measured concentrations is best for benzene and MTBE because there were no other major sources of either VOC in the study region. Conversely, Horn Pond Brook was not a major source of any of the other six VOCs simulated in this study.

A second similarity between benzene and MTBE is that both show an increase in concentration between the downstream end of zone 8c and the downstream end of zone 10. This increase in the measured surface-water concentrations indicates



**Figure 14.** Trichloroethene (TCE) in the Aberjona River showing (A) concentrations; (B) estimated source apportionment (SA) values for sources derived from synoptic survey; and (C) estimated SA values for sources chosen to provide best fit of TCE concentrations. Distance is measured going downstream (DS) from the upstream (US) end of zone 1 to the downstream end of zone 10 (see figure 6 for locations).



**Figure 15.** Perchloroethene (PCE) in the Aberjona River showing (A) concentrations; (B) estimated sources apportionment (SA) values for sources derived from synoptic survey; and (C) estimated SA values for sources chosen to provide best fit of PCE concentrations. Distance is measured going downstream (DS) from the upstream (US) end of zone 1 to the downstream end of zone 10 (see figure 6 for locations).

that there was a source for each VOC in those regions. Interestingly, in similarity with MTBE, the chlorinated compound PCE also shows a large increase in concentration in zones 9 and 10.

The major sources to the Aberjona River in the study area for the five chlorinated VOCs were due to ground-water inflows. Of these compounds, TCE yielded the best fit using the inputs derived from the synoptic data set. For 1,1-DCA and *cis*-1,2-DCE, the model results showed a similar trend between the simulated and the measured concentrations, although the absolute values of the simulated and measured concentrations differed on average by a factor of two for both compounds. For example, the synoptic-based inputs led to a decrease of about a factor of 2 in the simulated concentrations at the Aberjona/Horn Pond Brook confluence. Results for chloroform also showed a similar general trend between the simulated and measured concentrations, although it is evident that the simplistic estimate of  $m_{in,i}(GW)$  for zone 3 was too large. For PCE, it is evident that the estimated inputs clearly fail to adequately characterize the sources to the Aberjona River. It is also clear that in the case of the chlorinated compounds, the model consistently underestimates the measured VOC concentrations in zones 4 through 10 when using the VOC inputs derived directly from the synoptic study data (note that because of the large chloroform source in zone 3, only zones 8a through 10 are underestimated for that VOC). This indicates that there were missing source terms for these compounds in the synoptic study region.

The data in table 7 show the changes in VOC sources resulting from minimizing  $\chi^2$  defined in equation 48. The modified source data in table 7 can be used to look for commonalities in changes to VOC sources required to simulate their concentrations in the Aberjona River. Figure 16 shows the difference between the VOC source concentration yielding the best fit to the measured and source VOC concentrations derived from the synoptic data set normalized by the average concentration of that VOC,  $\beta_i$ , plotted for each zone in the Aberjona River (note that zone 3b is not shown because it was not assumed to be a source or sink of VOCs). In order to plot differences on a common scale, they have been normalized by the average VOC concentration over the synoptic study region as:

$$\beta_i = \frac{\Delta[\text{VOC}]_i}{[\text{VOC}]_{i,\text{AVG}}}, \quad (49)$$

where  $\Delta[\text{VOC}]_i$  is the difference between the modified source concentration and the best match source concentration determined from the synoptic study data set, and  $[\text{VOC}]_{i,\text{AVG}}$  is the average concentration of the VOC over the synoptic study zone.

For the sources in zones 1 through 7, the results in figure 16 show that one modification required for all of the VOCs modeled here except acetone was an increase in the strength of the VOC source in zone 5. This indicates that the synoptic study measurements did not identify a source of VOCs to the Aberjona River in this area. In addition to the missing source in zone 5, there also is some evidence that an additional source is required in zone 2 in the case of benzene, MTBE, chloroform, 1,1-DCA, TCE, and PCE. Finally, the optimization

increased the concentrations of benzene, chloroform, 1,1-DCA, *cis*-1,2-DCE, TCE, and PCE in Horn Pond Brook. These increases are consistent with the observation that the sources derived directly from the synoptic study data led to the model consistently underestimating VOC concentrations in the latter zones in the region.

The other common modifications required were in the synoptic study zones downstream from the confluence of the Aberjona River with Horn Pond Brook. These modifications required adding a large VOC source in zone 9 for the seven VOCs that were outgassing to reconcile the simulated loss of VOCs due to aeration at the weir. Similarly, MTBE, chloroform, 1,1-DCA, *cis*-1,2-DCE, TCE, and PCE required a large source in zone 8c to compensate for the VOC loss at the dam spillway.

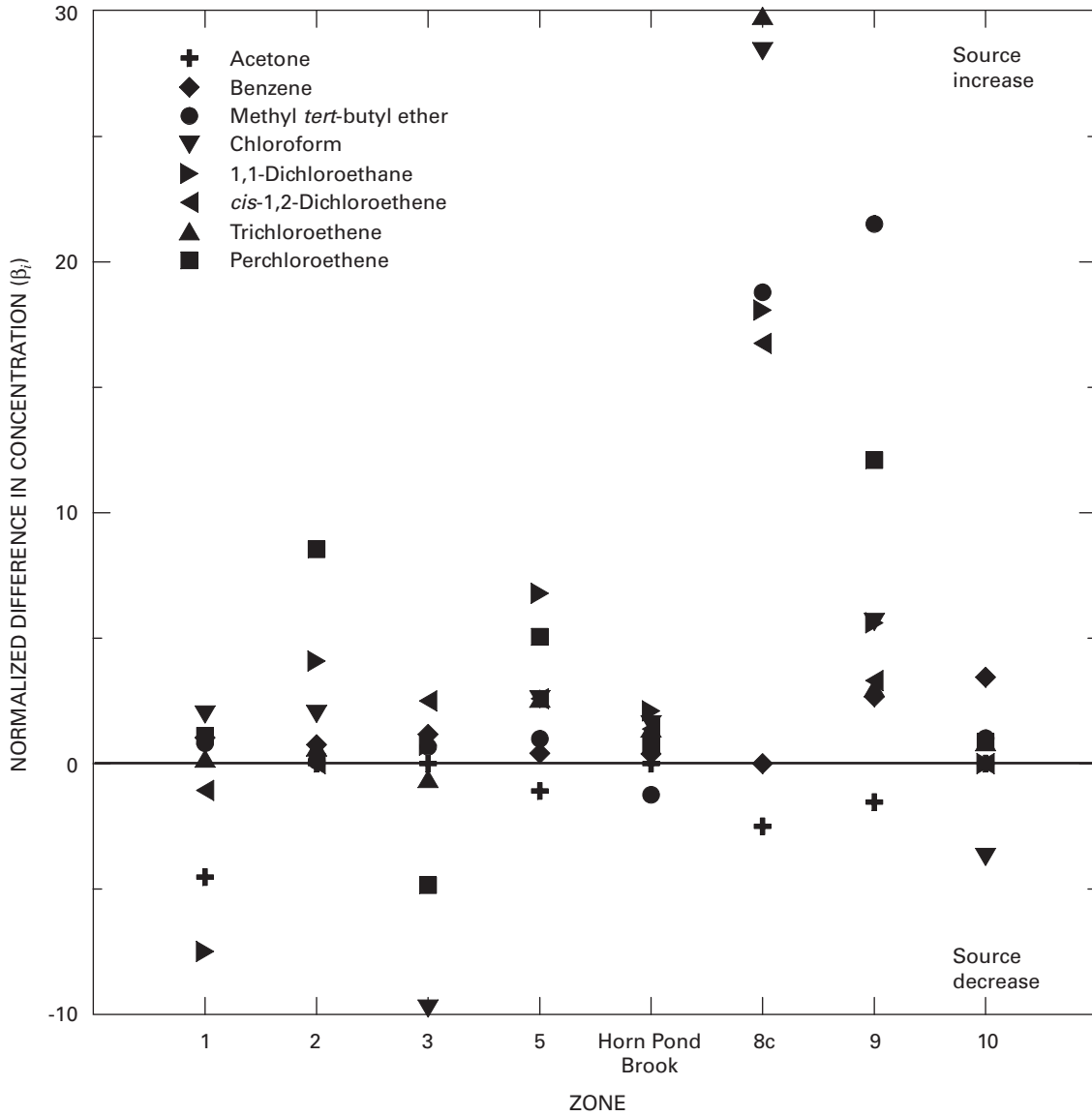
Flow under the dam and weir and the subsequent mixing as discussed previously could explain why the large decreases in VOC concentrations estimated by the optimization process using StreamVOC were not observed in measured concentrations. Assuming a value of  $\kappa$  typical for gravel (for example,  $\kappa = 0.01$  m/s) gave what could be considered as the largest reasonable estimate for  $F_{\text{under}}$ . Using this, the two structures on the Aberjona River in the synoptic study region were characterized by values of  $F_{\text{under}}$  of approximately 20 percent. This value for  $F_{\text{under}}$  was used in StreamVOC, and  $\chi_i^2$  defined in equation 48 was minimized to incorporate the effects of flow under the weir on the surface-water concentrations and inferred source strengths.

Figure 17 shows the fractional change in the concentration of the VOC sources in Horn Pond Brook and zones 8c, 9, and 10,  $\rho_{i,j}$ , defined as

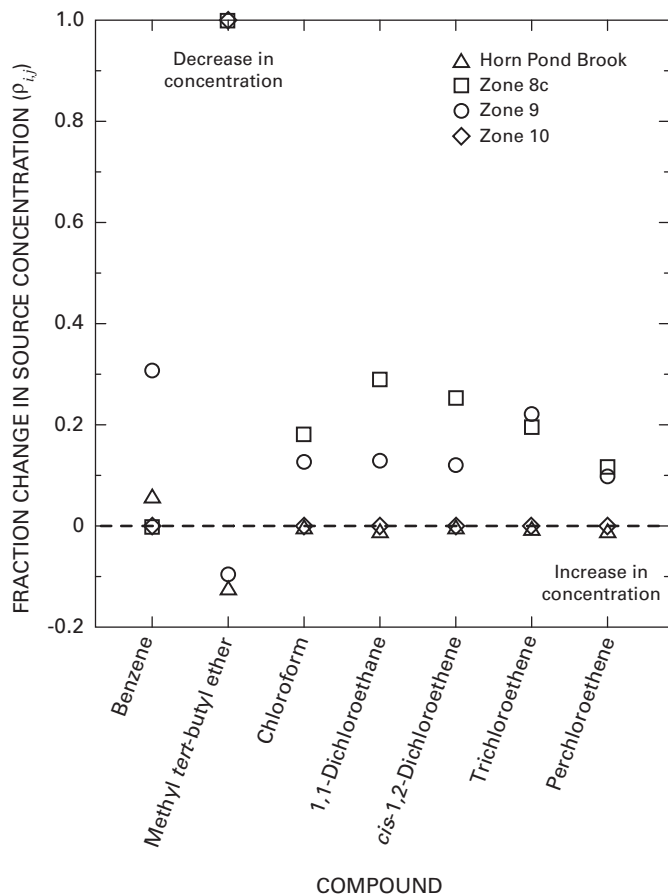
$$\rho_{i,j} = \frac{c_{i,j}(\text{no flow}) - c_{i,j}(\text{flow})}{c_{i,j}(\text{no flow})}, \quad (50)$$

where  $c_{i,j}(\text{no flow})$  is the optimized concentration of VOC  $i$  in source  $j$  assuming  $F_{\text{under}} = 0$ ; and  $c_{i,j}(\text{flow})$  is the optimized concentration of VOC  $i$  in source  $j$  assuming  $Q_{\text{under}}$  was  $0.2Q$ . We have defined  $\rho_{i,j} = 0$  for cases where  $c_{i,j}(\text{no flow})$  and  $c_{i,j}(\text{flow})$  are both zero although in a strict sense  $\rho_{i,j}$  is undefined. Acetone is not shown in figure 17 because there was no effect of including flow under the weir on the optimization. The  $\rho_{i,j}$  values show that except in the case of MTBE, in general the effect of including flow under the weir and dam is to decrease the concentration of  $c_{i,j}$  in zones 8c and 9 by a factor of 0.2 to 0.3. Furthermore, except in the case of MTBE, there is no effect of including flow under the weir on the source concentration of the VOCs in Horn Pond Brook and zone 10. It is not clear why the  $c_{\text{MTBE},j}(\text{flow})$  are so different from  $c_{\text{MTBE},j}(\text{no flow})$ . Figure 18A shows  $c_{\text{MTBE},j}(\text{flow})$  and  $c_{\text{MTBE},j}(\text{no flow})$ , and for comparison figure 18B shows  $c_{\text{TCE},j}(\text{flow})$  and  $c_{\text{TCE},j}(\text{no flow})$ , with the latter displaying the typical behavior of the other VOCs. Regardless of the details, the graphs of the concentrations show that for the VOCs included in the test model there is little effect of the flow under hydraulic structures on the downstream VOC concentrations.





**Figure 16.** The difference between the source volatile organic compound (VOC) concentration yielding the best fit to the measured VOC concentrations and the source VOC concentration derived from the synoptic data set normalized by the average concentration of that VOC,  $\beta_i$ , as defined in equation 49 as the difference between the modified source concentration and the source concentration determined from the synoptic study data set,  $\Delta[\text{VOC}]_i$ , divided by the average concentration of the VOC over the synoptic study zone,  $[\text{VOC}]_{i,AVG}$ , and plotted for each zone in the Aberjona River synoptic study region. Note that the zone positions on the x-axis are not drawn to scale and do not represent actual distances between the zones.



**Figure 17.** The fraction change in source concentration,  $\rho_{ij}$ , caused by including the effect of flow of surface water under the dam at the downstream end of zone 8c and the weir at the downstream end of zone 9 for the volatile organic compound sources in Horn Pond Brook and zones 8c, 9, and 10.  $\rho_{ij}$  is defined in equation 50 as the difference between the optimized VOC concentration assuming no flow under the dam or weir,  $c_{ij}(\text{no flow})$ , and the optimized VOC concentration assuming that 20 percent of the total streamflow was under a hydraulic structure,  $c_{ij}(\text{flow})$ , divided by  $c_{ij}(\text{no flow})$ .

Therefore, it is unlikely that flow under structures is the cause of the large sources in zones 8c and 9 generated by the optimization.

Although the addition of large sources in these zones seems unrealistic, all available experimental and theoretical studies indicate that weirs and spillways have a large effect on dissolved gas concentrations (McLachlan and others, 1990; Gulliver and others, 1998; Urban and others, 2001; Caplow and others, 2004). Additionally, there is no evidence that indicates that gas fluxes were severely overestimated at the hydraulic structures (for example, the aeration efficiencies estimated by StreamVOC are correct insofar as they are being correctly calculated by the relations given previously). Finally, there is some experimental evidence supporting the existence of large sources in this region—the measured surface-water concentrations for

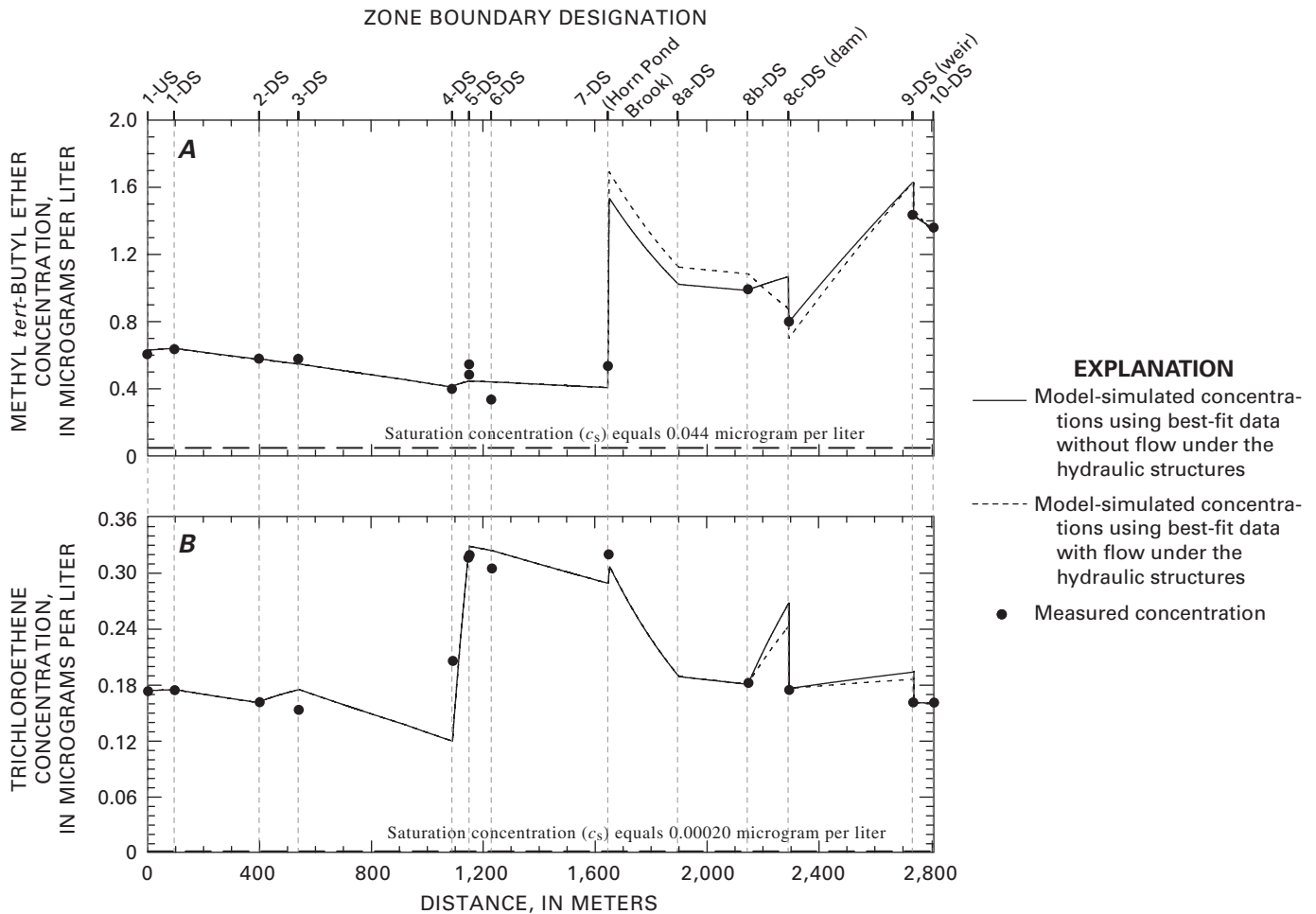
MTBE and PCE both show large increases over zones 8c and 9. But it also should be recognized that accurately estimating aeration at hydraulic structures from parameterizations such as used here is extremely difficult. Therefore, although there is no prior reason to assume that the VOC fluxes from the stream to the atmosphere due to the hydraulic structures are greatly overestimated by StreamVOC, the presence of large VOC sources in zones 8c and 9 is by no means certain based solely on the StreamVOC results.

VOC concentration measurements upstream and downstream from the weir and dam would provide evidence that the transfer efficiencies were being estimated correctly in the model. Because hydraulic structures can cause large changes in VOC concentrations, these additional concentration measurements also would help to parameterize VOC sources in a particular study region.

## Sensitivity Analyses

Field measurements of the VOC concentrations, streamflows, stream widths, and stream depths that are the primary input data to StreamVOC are subject to uncertainties and measurement errors. Furthermore, the accuracy of the input data will affect the values calculated by the model. In order to assess this effect on the model output, a sensitivity study was conducted using the optimized source input concentrations,  $c_{ij}$ , listed in table 7. The variation of the model-simulated surface-water concentrations was calculated for changes in  $c_{ij}$ ,  $h$ ,  $w$ , and  $Q$ . The variation was calculated by running StreamVOC with the value of a variable in a zone increased by 10 percent, and a second simulation was run where the value was decreased by 10 percent. This was done on an individual basis so that in the case of  $h$ , for example, a total of 20 separate model runs were conducted. The maximum and minimum concentrations resulting from these calculations are shown in figures 19–26 for the eight VOCs included in the test model.

The results for the sensitivity analyses show that variations in source concentrations have the largest effect on the surface-water concentrations, followed by the source flows, with the effect of width and depth being relatively minor. Replicate samples are only available from the downstream end of zone 5. Furthermore, because only two replicates were collected, it is not possible to compute a standard deviation from the data at a single location. However, the point samples from the downstream ends of zones 4, 5, and 6 are all within 140 m of each other and combined they can be used to estimate concentration variances for each compound (except in the case of benzene, where only one concentration was measured to be above the MDL). The standard deviation is 24 percent of the mean for acetone, 20 percent for MTBE, 12 percent for chloroform, 8.5 percent for 1,1-DCA, 6.2 percent for *cis*-1,2-DCE, 18 percent for TCE, and 15 percent for PCE. By comparing the range of concentrations given by these standard deviations with the range of concentrations generated by StreamVOC based on the sensitivity test, it is seen that the sensitivity of the model is less than the



**Figure 18.** Model-simulated surface-water concentrations of (A) methyl *tert*-butyl ether for the condition where there is no flow of surface water under the hydraulic structures,  $c_{\text{MTBE}}(\text{no flow})$ , and when there is flow under the structure,  $c_{\text{MTBE}}(\text{flow})$ ; and (B) trichloroethene assuming no flow under the weir and flow under the weir,  $c_{\text{TCE}}(\text{no flow})$ , and  $c_{\text{TCE}}(\text{flow})$ , respectively.

variance in the measured concentrations. This indicates that most of the larger changes in concentration as a function of sampling site observed in the surface-water synoptic study samples are not due solely to experimental noise and that the optimized source strengths could reflect the presence of sources not adequately accounted for using only the ground-water inflows determined from the synoptic study data set.

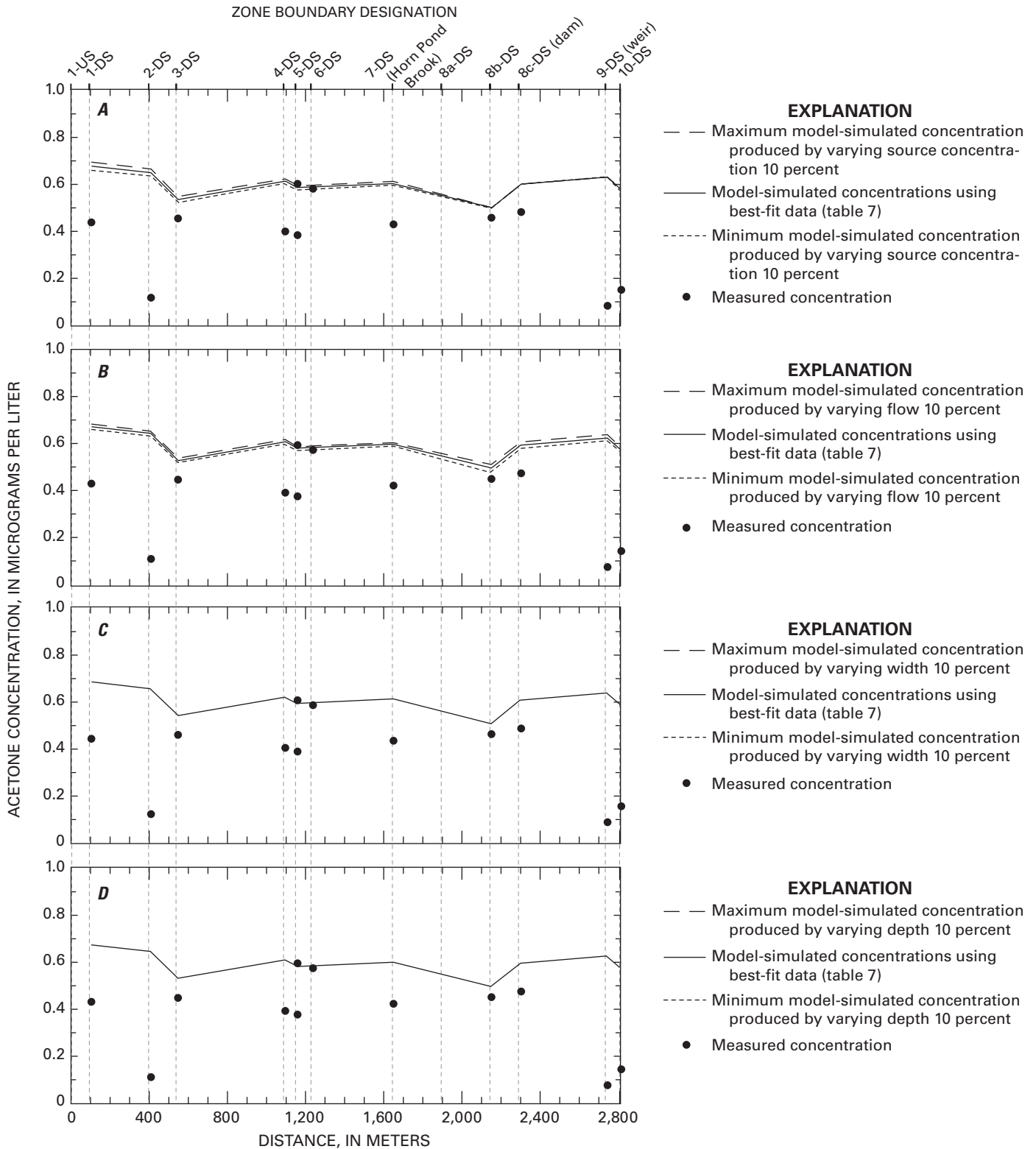
The assumption that the sources were distributed evenly over zones where the net streamflow increased is a simplification. It is understood that the distribution of sources in a zone could be a combination of small point sources and distributed sources that extend only over part of a zone. Although there is no best way to model a more complicated set of sources given the limitations of the source synoptic study data set, it is possible to determine whether the distribution of sources used here is a reasonable approximation to the true distribution of sources. Figure 27 shows the normalized difference between the measured and model-simulated concentrations (the modeled concentration was calculated using the optimized source inputs),  $\gamma_{i,j}$ , defined as

$$\gamma_{i,j} = \frac{[\text{VOC}]_{i,j,\text{MEASURED}} - [\text{VOC}]_{i,j,\text{MODEL-SIMULATED}}}{[\text{VOC}]_{i,\text{AVG}}} \quad (51)$$

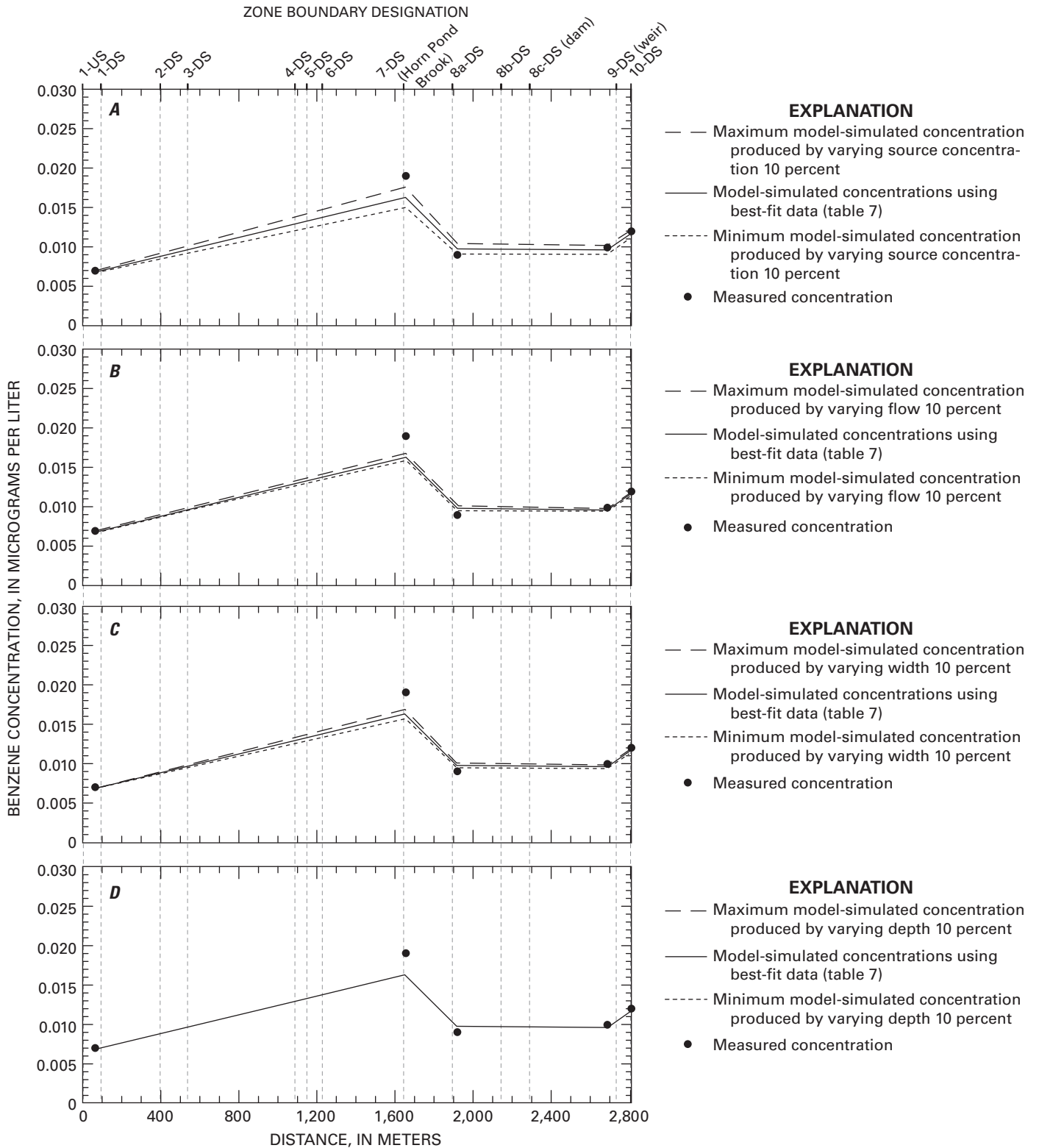
plotted by zone number. In most cases, the values for  $\gamma_{i,j}$  are scattered around zero, showing that there is no systematic pattern of overestimation or underestimation of the measured concentrations. However, there is some indication that the VOC concentrations at the downstream end of zone 4 were consistently underestimated, indicating the presence of a VOC source in the zone. Because zone 4 was a region where streamflow decreased, it was not possible to include a VOC source in this region using the assumption of continuous sources over an entire zone.

## Model Limitations and Program Considerations

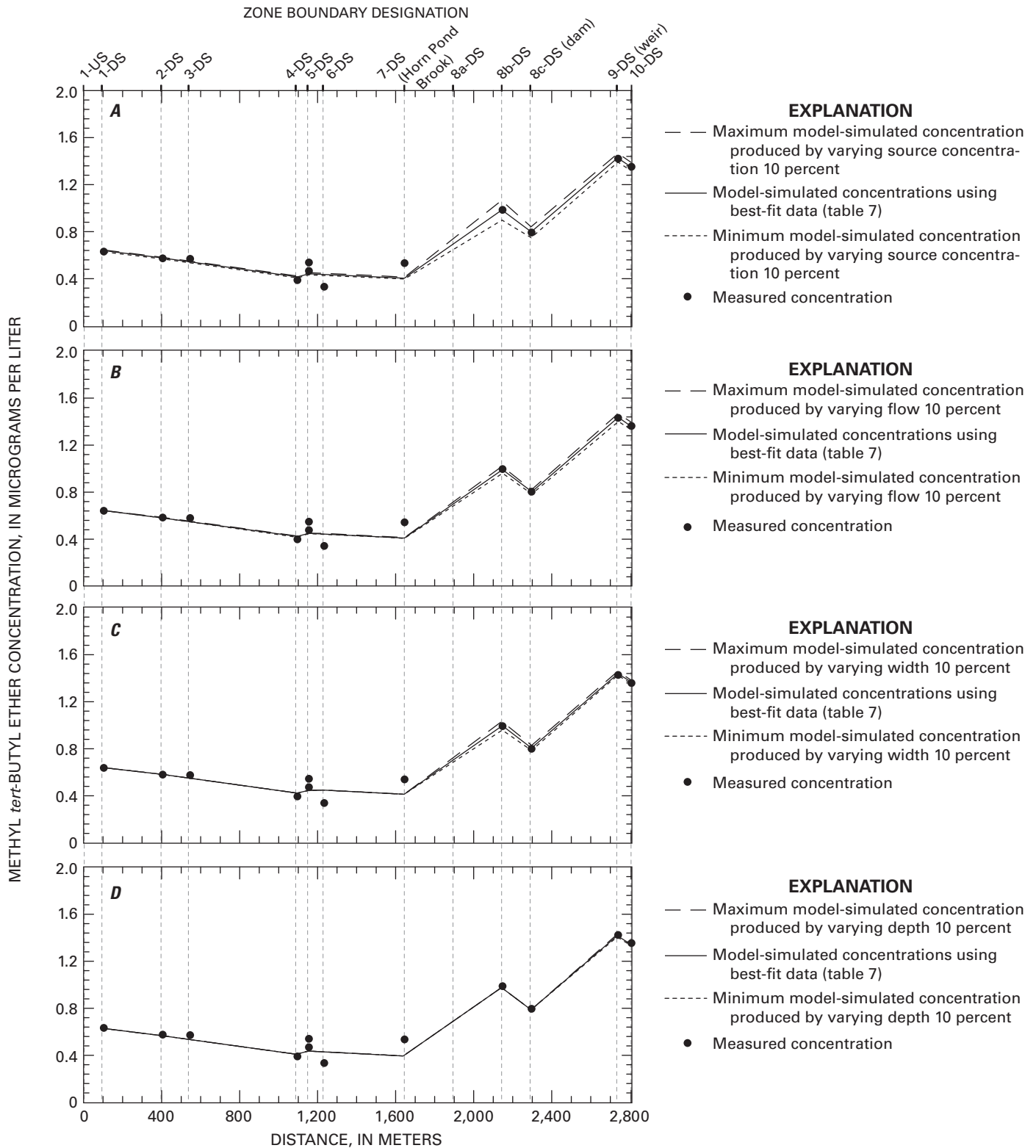
The results obtained in this study illustrate the great utility of SA concepts when seeking to (1) understand and identify the sources and sinks acting to determine location-dependent concentrations of contaminants in surface waters; and (2) determine potential courses of action for remediation and source



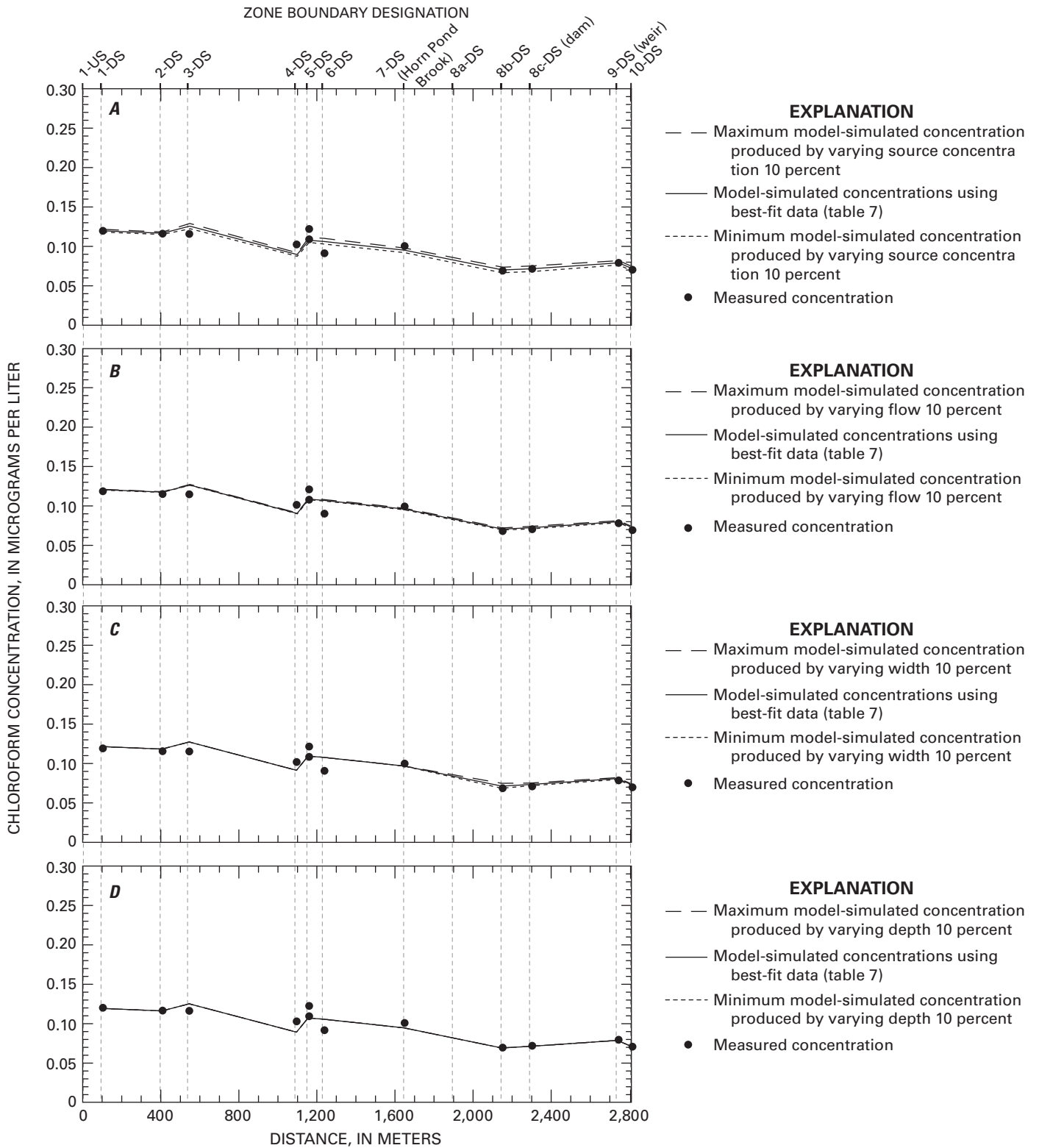
**Figure 19.** Results of model sensitivity analyses done for acetone using StreamVOC and the acetone sources determined from the source synoptic study data set by varying (A) the concentration of the individual acetone sources; (B) the flow volumes of the ground-water sources in each zone and in Horn Pond Brook; (C) stream width in each zone; and (D) stream depth in each zone.



**Figure 20.** Results of model sensitivity analyses done for benzene using StreamVOC and the benzene sources determined by minimizing the reduced chi-square value between the measured surface-water concentrations and concentrations calculated using StreamVOC by varying (A) the concentration of the individual benzene sources; (B) the flow volumes of the ground-water sources in each zone and in Horn Pond Brook; (C) stream width in each zone; and (D) stream depth in each zone.

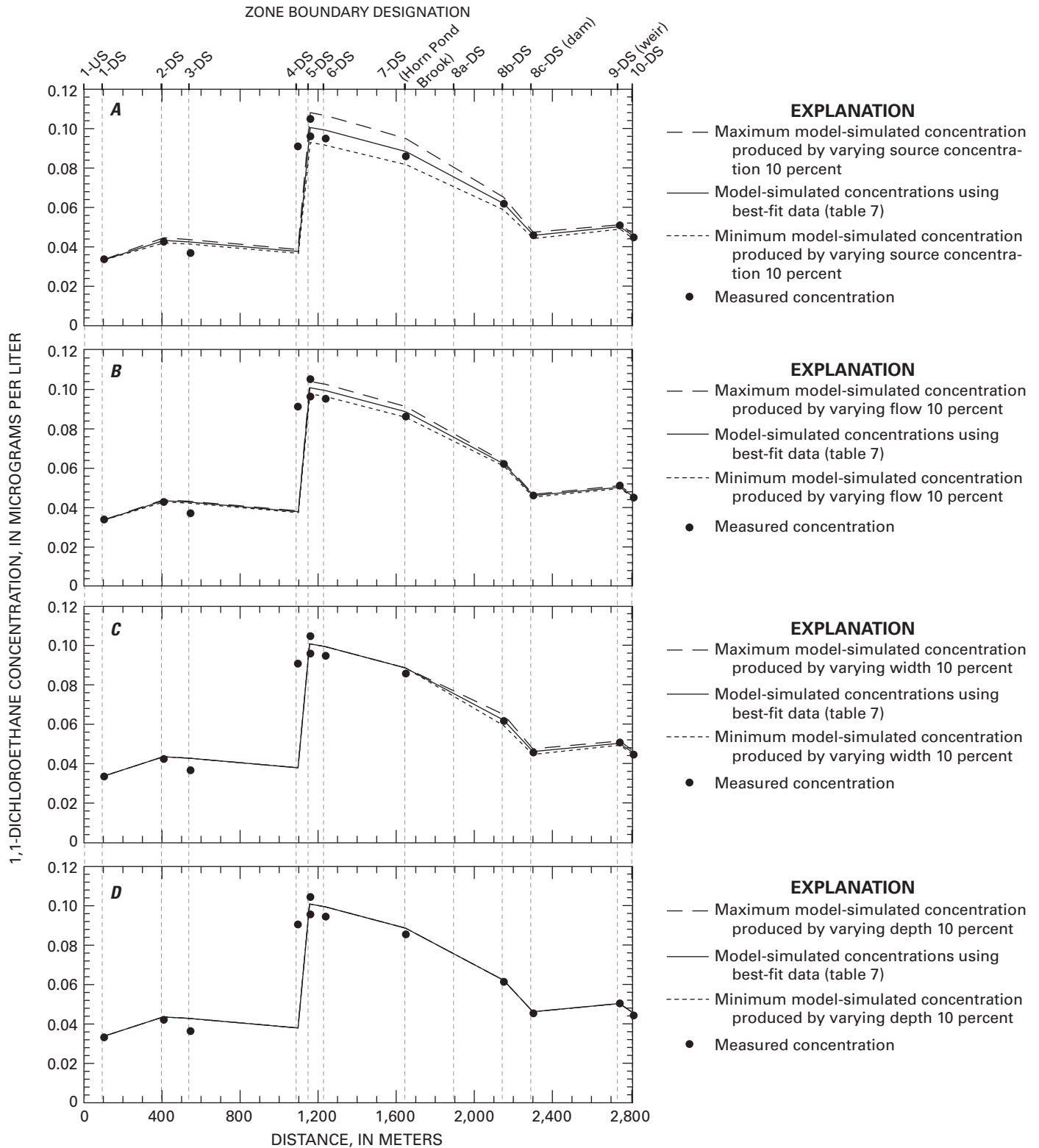


**Figure 21.** Results of model sensitivity analyses done for methyl *tert*-butyl ether (MTBE) using StreamVOC and the MTBE sources determined by minimizing the reduced chi-square value between the measured surface-water concentrations and concentrations calculated using StreamVOC by varying (A) the concentration of the individual MTBE sources; (B) the flow volumes of the ground-water sources in each zone and in Horn Pond Brook; (C) stream width in each zone; and (D) stream depth in each zone.



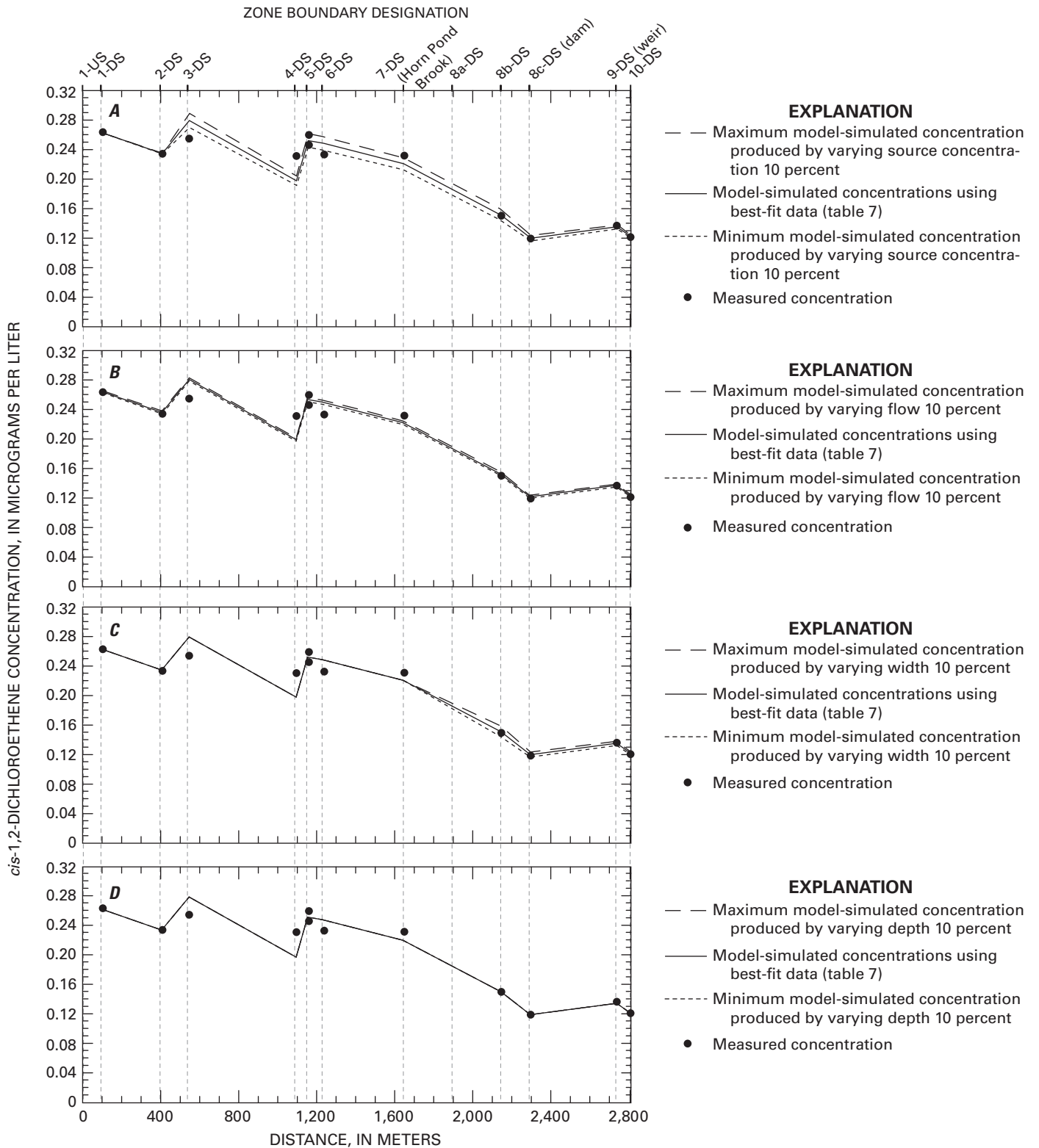
**Figure 22.** Results of model sensitivity analyses done for chloroform using StreamVOC and the chloroform sources determined by minimizing the reduced chi-square value between the measured surface-water concentrations and concentrations calculated using StreamVOC by varying (A) the concentration of the individual chloroform sources; (B) the flow volumes of the ground-water sources in each zone and in Horn Pond Brook; (C) stream width in each zone; and (D) stream depth in each zone.



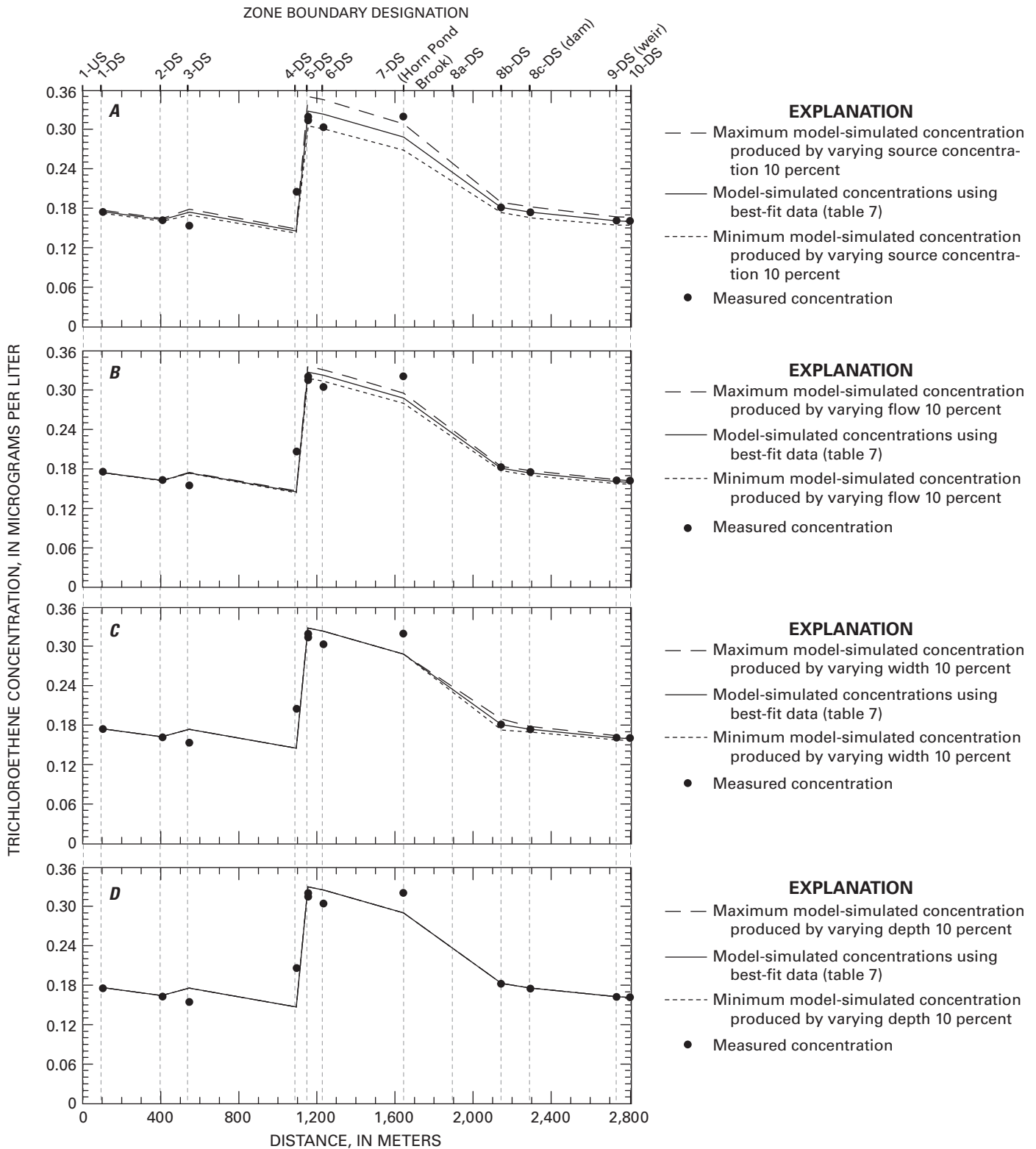


**Figure 23.** Results of model sensitivity analyses done for 1,1-dichloroethane (1,1-DCA) using StreamVOC and the 1,1-DCA sources determined by minimizing the reduced chi-square value between the measured surface-water concentrations and concentrations calculated using StreamVOC by varying (A) the concentration of the individual 1,1-DCA sources; (B) the flow volumes of the ground-water sources in each zone and in Horn Pond Brook; (C) stream width in each zone; and (D) stream depth in each zone.

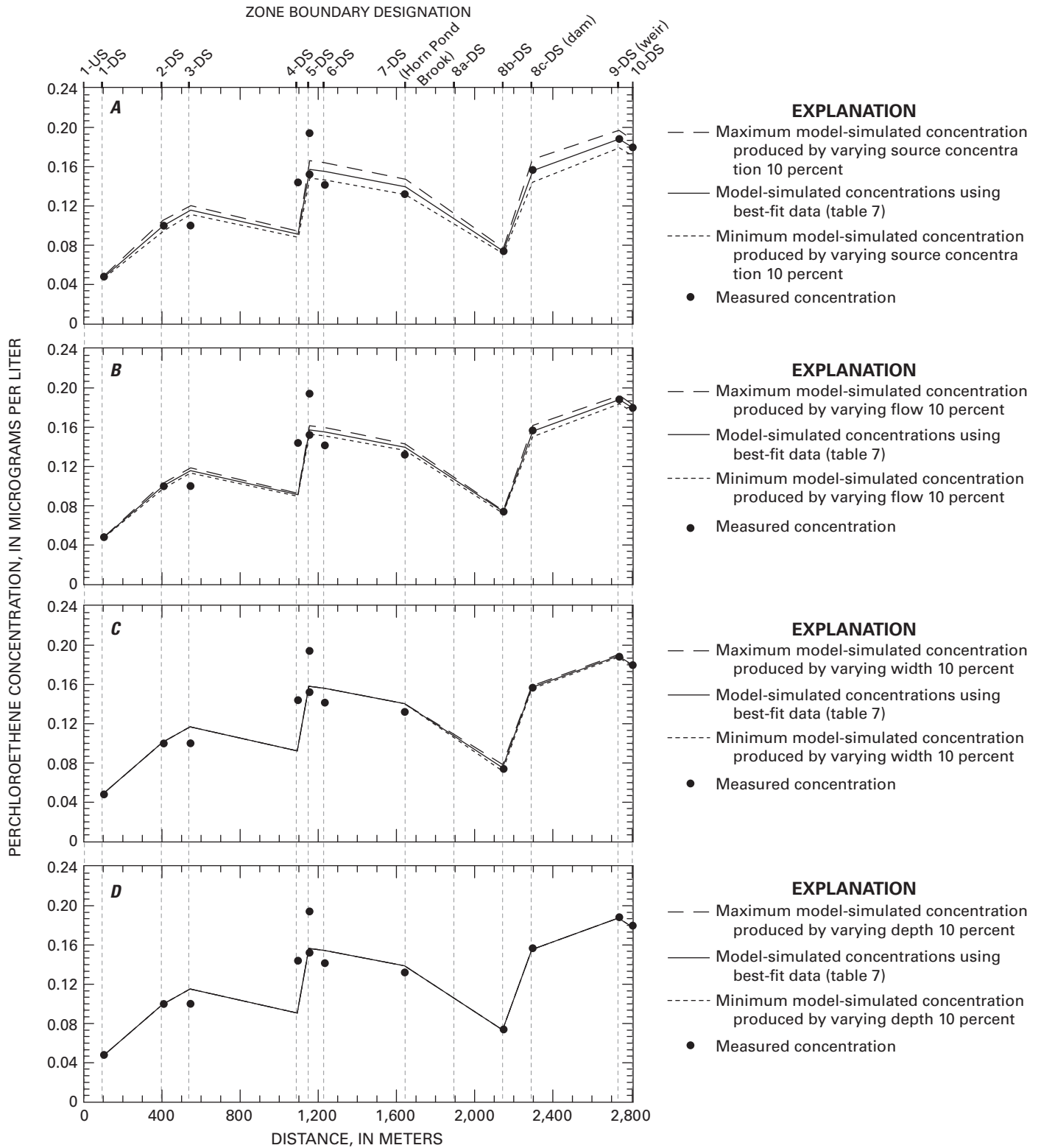




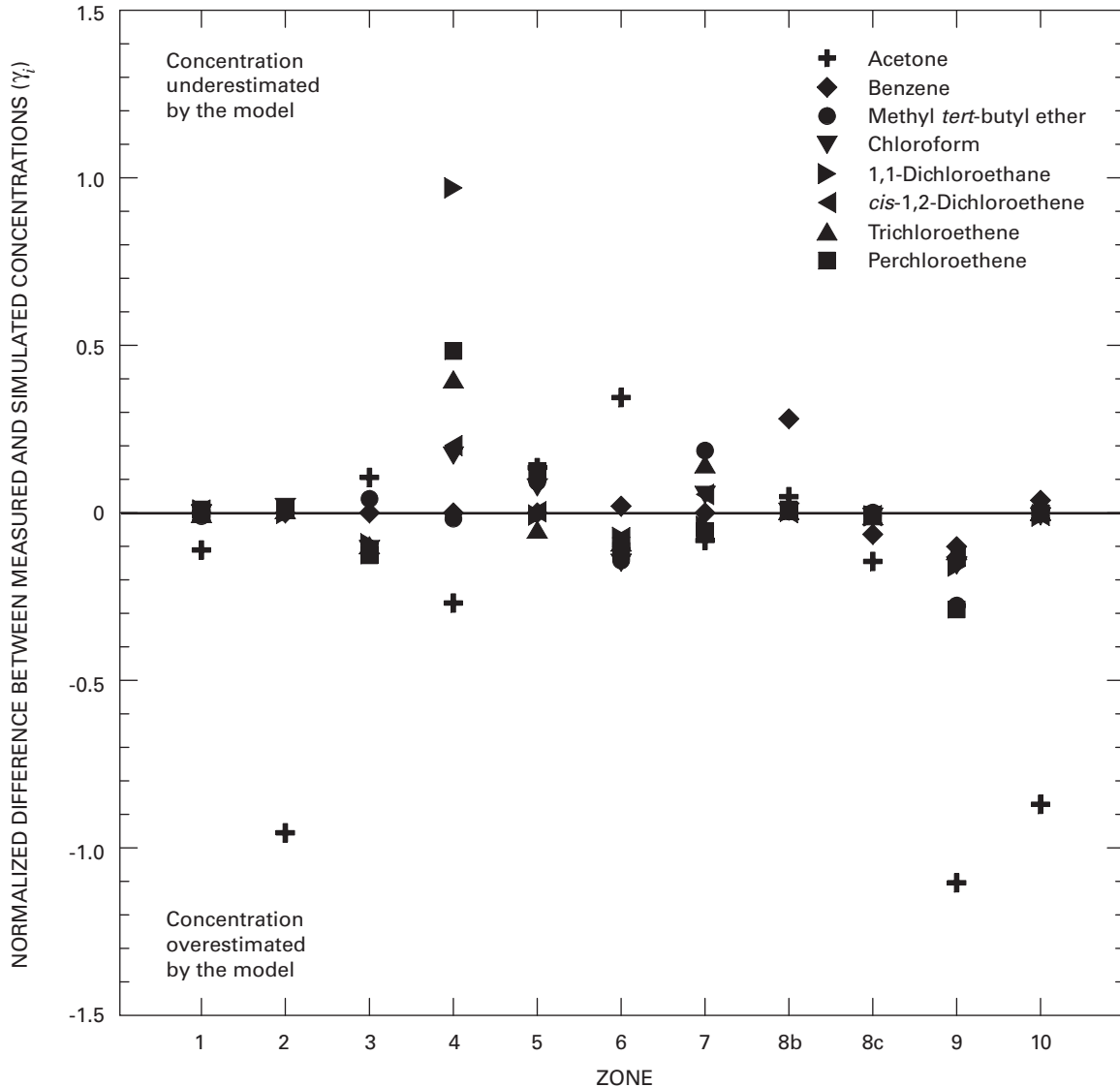
**Figure 24.** Results of model sensitivity analyses done for *cis*-1,2-dichloroethene (*cis*-1,2-DCE) using StreamVOC and the *cis*-1,2-DCE sources determined by minimizing the reduced chi-square value between the measured surface-water concentrations and concentrations calculated using StreamVOC by varying (A) the concentration of the individual *cis*-1,2-DCE sources; (B) the flow volumes of the ground-water sources in each zone and in Horn Pond Brook; (C) stream width in each zone; and (D) stream depth in each zone.



**Figure 25.** Results of model sensitivity analyses done for trichloroethene (TCE) using StreamVOC and the TCE sources determined by minimizing the reduced chi-square value between the measured surface-water concentrations and concentrations calculated using StreamVOC by varying (A) the concentration of the individual TCE sources; (B) the flow volumes of ground-water sources in each zone and in Horn Pond Brook; (C) stream width in each zone; and (D) stream depth in each zone.



**Figure 26.** Results of model sensitivity analyses done for perchloroethene (PCE) using StreamVOC and the PCE sources determined by minimizing the reduced chi-square value between the measured surface-water concentrations and concentrations calculated using StreamVOC by varying (A) the concentration of the individual PCE sources; (B) in the flow volumes of the ground-water sources in each zone and in Horn Pond Brook; (C) stream width in each zone; and (D) stream depth in each zone.



**Figure 27.** The normalized difference between the volatile organic compound (VOC) concentration measured in the Aberjona River and the VOC concentration simulated by the model using the optimized sources,  $\gamma_{ij}$  as defined in equation 51 as the difference between the measured and model-simulated concentrations divided by the average concentration over the synoptic study zone, and plotted for each zone in the Aberjona River source synoptic study region. Note that the zone positions on the x-axis are not drawn to scale and do not represent actual distances between the zones.

reduction in an effort to lower VOC concentrations in streams. For example, based on model results and subject to model limitations, reducing the MTBE and benzene contamination of Horn Pond Brook would be required in order to reduce the concentrations of these compounds in the downstream portion of the study section. As another example, for *cis*-1,2-DCE as simulated using the inputs determined from the synoptic data set, the source fractions show that at the downstream end of the study interval, more than 50 percent of the compound in the river is due to the initial inflow entering at the upstream end of zone 1. Thus, remediation of all *cis*-1,2-DCE sources along the

study interval could reduce the concentrations by, at most, a factor of two.

In general, this study illustrated (1) the considerable difficulty of quantifying correctly the locations and magnitudes of ground-water-related sources of contamination in streams; and (2) that model-based estimates of stream VOC concentrations are likely to be most accurate when the major sources are point sources or tributaries where the spatial extent and magnitude of the sources are tightly constrained and easily determined.

## Summary

The National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey seeks to understand the sources and processes that determine the concentrations, transport, and fate of contaminants in the natural waters of the United States. Contaminant groups of interest include volatile organic compounds (VOCs), and for urban streams, NAWQA results indicate the frequent presence of multiple dissolved VOCs. An adequate understanding, however, does not exist of the identities and relative roles of the typical contaminant sources that lead to the observed VOC concentrations, nor 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. There is interest in the continued development of “source apportionment” (SA) modeling principles for use in tracking 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 to VOC concentrations include the need to apportion: (1) the origins for observed contamination, and (2) the associated human and ecosystem risks.

This report documents the construction and verification of the model, StreamVOC, that estimates (1) the time- and position-dependent concentrations of volatile organic compounds (VOCs) in rivers and streams as well as (2) the source apportionment (SA) of those concentrations. The model considers how different types of sources and loss processes can act together to yield a given observed VOC concentration. For VOCs, sources of interest include the atmosphere (by absorption), as well as point and nonpoint inflows of VOC-containing water. Loss processes of interest include volatilization to the atmosphere, degradation, and outflows of VOC-containing water from the stream to local ground water.

This report presents the details of StreamVOC and compares model output with measured concentrations for eight VOCs—acetone, benzene, methyl *tert*-butyl ether (MTBE), chloroform, 1,1-dichloroethane, *cis*-1,2-dichloroethene (*cis*-1,2-DCE), trichloroethene, and perchloroethene—found in the Aberjona River at Winchester, Massachusetts. Input data for the model were obtained during a synoptic study of the stream system conducted July 11–13, 2001, as part of the NAWQA Program of the U.S. Geological Survey. The input data included a variety of basic stream characteristics (for example, flows, temperature, and VOC concentrations).

The StreamVOC concentration results agreed moderately well with the measured concentration data for several VOCs and provided compound-dependent SA estimates as a function of longitudinal distance down the river. For many VOCs, the quality of the agreement between the model-simulated and measured concentrations could be improved by simple adjustments of the model input parameters.

The results obtained in this study illustrate the great utility of SA concepts when seeking to (1) understand and identify the

sources and sinks acting to determine location-dependent concentrations of contaminants in surface waters; and (2) determine potential courses of action for remediation and source reduction in an effort to lower VOC concentrations in streams. In general, this study illustrated (1) the considerable difficulty of quantifying correctly the locations and magnitudes of ground-water-related sources of contamination in streams; and (2) that model-based estimates of stream VOC concentrations are likely to be most accurate when the major sources are point sources or tributaries where the spatial extent and magnitude of the sources are tightly constrained and easily determined.

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## **Appendixes**

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