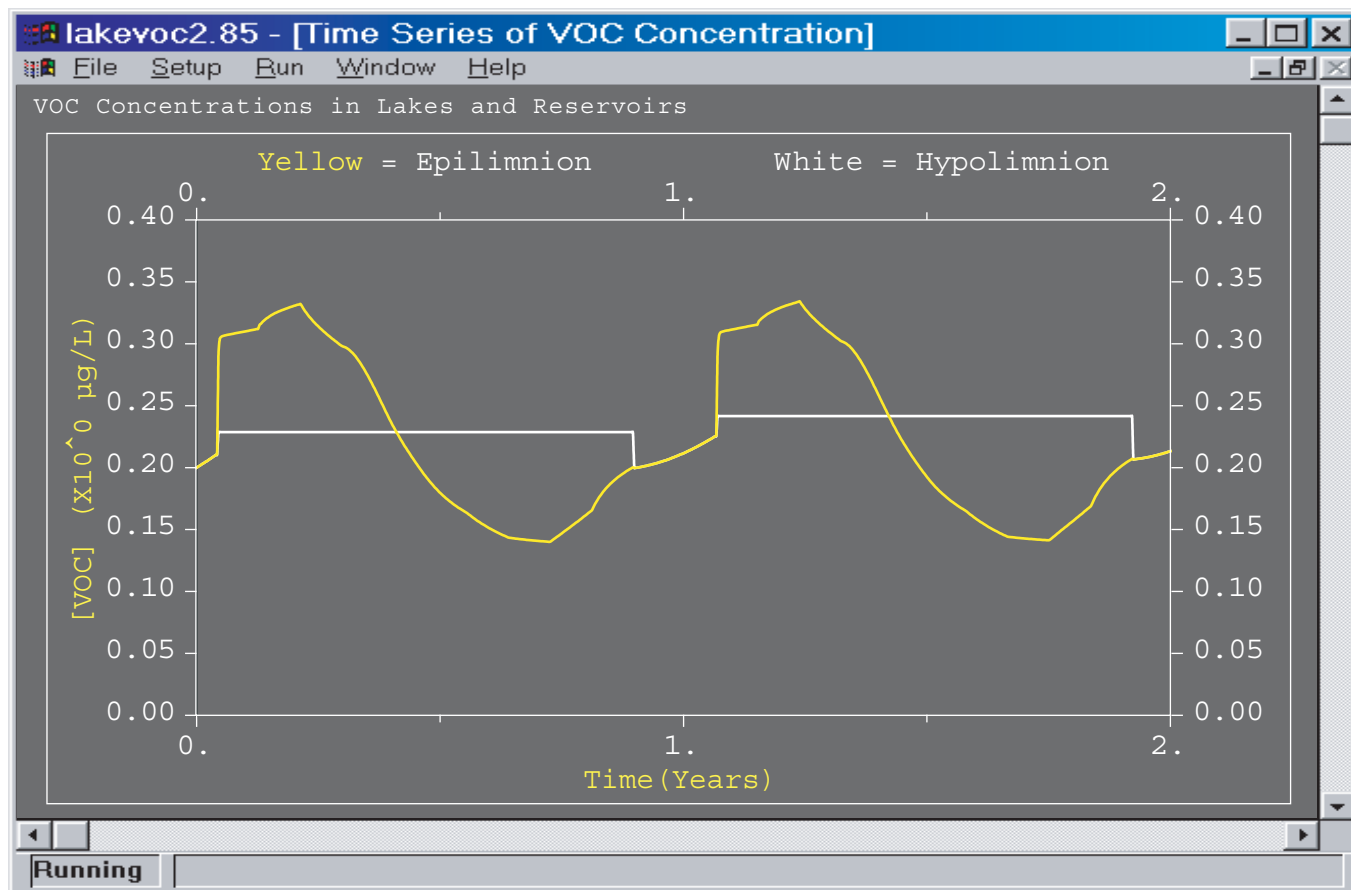


**NATIONAL WATER-QUALITY ASSESSMENT PROGRAM
NATIONAL SYNTHESIS ON VOLATILE ORGANIC COMPOUNDS**

LakeVOC—A Deterministic Model to Estimate Volatile Organic Compound Concentrations in Reservoirs and Lakes

Open-File Report 03-212



LakeVOC—A Deterministic Model to Estimate Volatile Organic Compound Concentrations in Reservoirs and Lakes

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

Open-File Report 03-212

U.S. Department of the Interior

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FOREWORD

The U.S. Geological Survey (USGS) is committed to providing the Nation with accurate and timely scientific information that helps enhance and protect the overall quality of life and that facilitates effective management of water, biological, energy, and mineral resources (<http://www.usgs.gov/>). Information on the quality of the Nation's water resources is critical to assuring the long-term availability of water that is safe for drinking and recreation and suitable for industry, irrigation, and habitat for fish and wildlife. Population growth and increasing demands for multiple water uses make water availability, now measured in terms of quantity and quality, even more essential to the long-term sustainability of our communities and ecosystems.

The USGS implemented the National Water-Quality Assessment (NAWQA) Program in 1991 to support national, regional, and local information needs and decisions related to water-quality management and policy (<http://water.usgs.gov/nawqa>). Shaped by and coordinated with ongoing efforts of other Federal, State, and local agencies, the NAWQA Program is designed to answer: What is the condition of our Nation's streams and ground water? How are the conditions changing over time? How do natural features and human activities affect the quality of streams and ground water, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues and priorities.

From 1991-2001, the NAWQA Program completed interdisciplinary assessments in 51 of the Nation's major river basins and aquifer systems, referred to as Study Units (<http://water.usgs.gov/nawqa/studyu.html>). Baseline conditions were established for comparison to future assessments, and long-term monitoring was initiated in many of the basins. During the next decade, 42 of the 51 Study

Units will be reassessed so that 10 years of comparable monitoring data will be available to determine trends at many of the Nation's streams and aquifers. The next 10 years of study also will fill in critical gaps in characterizing water-quality conditions, enhance understanding of factors that affect water quality, and establish links between sources of contaminants, the transport of those contaminants through the hydrologic system, and the potential effects of contaminants on humans and aquatic ecosystems.

The USGS aims to disseminate credible, timely, and relevant science information to inform practical and effective water-resource management and strategies that protect and restore water quality. We hope this NAWQA publication will provide you with insights and information to meet your needs, and will foster increased citizen awareness and involvement in the protection and restoration of our Nation's waters.

The USGS recognizes that a national assessment by a single program cannot address all water-resource issues of interest. External coordination at all levels is critical for a fully integrated understanding of watersheds and for cost-effective management, regulation, and conservation of our Nation's water resources. The NAWQA Program, therefore, depends on advice and information from other agencies—Federal, State, interstate, Tribal, and local—as well as nongovernmental organizations, industry, academia, and other stakeholder groups. Your assistance and suggestions are greatly appreciated.

Robert M. Hirsch
Associate Director for Water

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SYMBOLS, UNITS OF MEASUREMENT, AND ABBREVIATIONS

<u>Symbol</u>	<u>Description</u>	<u>Units of measurement</u>
α	Ostwald solubility coefficient	
δ	volume mass balance term	m^3/day
δ_E	epilimnion mass-balance term	mol/day
ΔC	air-water concentration difference	mol/m^3
ε	evaporation rate	m^3/day
ε_T	Runge-Kutta tolerance	dimensionless
λ_E	biochemical degradation rate in the epilimnion	mol/day
λ_H	biochemical degradation rate in the hypolimnion	mol/day
μ	absolute viscosity of water	$(\text{g}/\text{cm})/\text{s}$
ν	kinematic viscosity of water	cm^2/s
Φ	general exchange term	m^3/day
Φ_{EH}	flow of water from the epilimnion to the hypolimnion	m^3/day
Φ_{HE}	flow of water from the hypolimnion to the epilimnion	m^3/day
A, B, C, D	Wanninkhof (1992) coefficients for Sc	
A_0, B_0	Robbins and others (1993) coefficients for H	
$A_1, A_2, A_3,$ B_1, B_2, B_3	Wanninkhof (1992) coefficients for H	
A_L	lake-surface area	m^2
$A_{L(z)}$	lake-surface area in relation to depth profile	
C_0	initial concentration	mol/m^3
C_A	atmospheric concentration	ppbv
C_E	concentration in the epilimnion	mol/m^3
C_H	concentration in the hypolimnion	mol/m^3
C_S	saturation concentration	mol/m^3
D_E	epilimnion depth	meters
$D_G(H_2O)$	air-phase diffusivity of water	cm^2/s
$D_G(VOC)$	air-phase diffusivity of volatile organic compound	cm^2/s
D_L	aqueous-phase molecular diffusivity	cm^2/s
DO	dissolved oxygen	mg/L
D_T	total lake depth	meters
F	net flux	$\text{mol}/\text{m}^2\text{-s}$
h	thickness of the layer	meters
H	Henry's law coefficient	$\text{atm}\text{-m}^3/\text{mol}$
H_I	inflow height	meters
H_O	outflow height	meters
I_E	inflow to the epilimnion	m^3/day
I_H	inflow to the hypolimnion	m^3/day

k_{OL}	liquid-side overall mass transfer velocity	m/s
k_L	transfer velocity through the water-side layer	m/s
k_G	transfer velocity through the air-side layer	m/s
$k_G(H_2O)$	gas-side transfer velocity for water	m/s
L_I	lake inflow volume	m ³ /day
L_O	lake outflow volume	m ³ /day
M_{IN}	input from motorboats or other sources	mol/day
M_T	total mass in the lake	mol/m ³
M_{VOC}	molecular weight	g/mol
N_A	number of points in $A_{L(z)}$	
N_E	number of layers in the epilimnion	
N_H	number of layers in the hypolimnion	
O_E	outflow from the epilimnion	m ³ /day
O_H	outflow from the hypolimnion	m ³ /day
P_A	partial pressure	atm
P_{atm}	atmospheric pressure	atm
r_1	radius of the top layer	meters
r_2	radius of the bottom layer	meters
r_N	radius at layer N	meters
R	universal gas constant	m ³ -atm/K-mol
R_H	relative humidity	percent
S	salinity	parts per thousand (ppt)
Sc	Schmidt number	dimensionless
T_O	data output time step	day
T_A	air temperature	Kelvin, K; degree Celsius, °C
T_S	total simulation time	year
T_W	water temperature	Kelvin, K; degree Celsius, °C
U_{10}	wind speed at 10 meters above water surface	m/s
V_E	volume of the epilimnion	m ³
V_H	volume of the hypolimnion	m ³
V_L	volume of conical layer	m ³
V_M	molar volume at the normal boiling point	cm ³ /mol
VOC	volatile organic compound	
V_P	vapor pressure of water	Pa
V_T	total volume of the lake	m ³
z_N	lake depth at layer N	meters
μg	microgram	
$\mu\text{g/L}$	microgram per liter	
atm	atmosphere	
atm-m ³ /mol	atmosphere-cubic meter per mole	

cm^2/s	square centimeter per second
cm^3/mol	cubic centimeter per mole
$^{\circ}\text{C}$	degree Celsius
$(\text{g}/\text{cm})/\text{s}$	gram per centimeter per second
$(\text{g}/\text{d})/\text{m}^2$	gram per day per square meter
g/mole	gram per mole
kg	kilogram
kg/d	kilogram per day
kg/wk	kilogram per week
kg/mon	kilogram per month
K	degree Kelvin
m	meter
m^2	square meter
m^3	cubic meter
m^3/d	cubic meter per day
m^3/wk	cubic meter per week
m^3/mon	cubic meter per month
m/s	meter per second
m/d	meter per day
mg/L	milligram per liter
mL/mole	milliliter per mole
mm	millimeter
mm/d	millimeter per day
mol/day	moles per day
$\text{mol}/\text{m}^2\text{-s}$	mole per square meter per second
mol/m^3	moles per cubic meter
ppbv	part per billion by volume
ppt	parts per thousand
Pa	pascal
$\text{Pa}\text{-m}^3/\text{mol}$	pascals-cubic meter per mole

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

ABSTRACT

This report documents LakeVOC, a model to estimate volatile organic compound (VOC) concentrations in lakes and reservoirs. LakeVOC represents the lake or reservoir as a two-layer system and estimates VOC concentrations in both the epilimnion and hypolimnion. The air-water flux of a VOC is characterized in LakeVOC in terms of the two-film model of air-water exchange. LakeVOC solves the system of coupled differential equations for the VOC concentration in the epilimnion, the VOC concentration in the hypolimnion, the total mass of the VOC in the lake, the volume of the epilimnion, and the volume of the hypolimnion.

A series of nine simulations were conducted to verify LakeVOC representation of mixing, dilution, and gas exchange characteristics in a hypothetical lake, and two simulations were conducted to verify LakeVOC estimates of VOC concentrations in an actual reservoir under environmental conditions. These 11 simulations showed that LakeVOC correctly handled mixing, dilution, and gas exchange and adequately estimated VOC concentrations within the epilimnion in an actual reservoir with daily input parameters. As the parameter-input time scale increased (from daily

to weekly to monthly, for example), the differences between the measured-averaged concentrations and the model-estimated concentrations generally increased, especially for the hypolimnion. This may be because as the time scale is increased from daily to weekly to monthly, the averaging of model inputs may cause a loss of detail in the model estimates.

INTRODUCTION

Lakes and reservoirs are important sources of drinking water and are used extensively for recreational purposes. On the basis of information in the United States Environmental Protection Agency's Safe Drinking Water Information System database, approximately 124 million people in the United States (47 percent of the population served by public water supplies) are served by public water suppliers where the source(s) of water include lakes and reservoirs (Marilee A. Horn, U.S. Geological Survey, written commun., August 26, 2002). Of the 124 million people served by public water supplies where the source is from lakes or reservoirs, approximately 34 million are using lakes or reservoirs as the sole source of water (Marilee A. Horn, U.S. Geological Survey, written commun., August 26, 2002). Recreational activities on

lakes and reservoirs include swimming, fishing, water skiing, boating, sailing, racing, and wind surfing. Because many lakes and reservoirs are used as drinking-water sources, there is a need for a simplified tool to estimate the levels of contaminants from recreational activities and to evaluate management options.

Volatile organic compounds (VOCs), including methyl *tert*-butyl ether (MTBE), have been found in lakes and reservoirs in the northeastern United States (Baehr and Zapecza, 1998; Baehr and Reilly, 2001), Lake Tahoe, Nevada and California (Boughton and Lico, 1998; Lico and Pennington, 1999), California (Reuter and others, 1998; Dale and others, 2000), and Texas (Mahler, 2000). VOCs have also been found in European lakes and reservoirs (Jüttner, 1988; van Donkelaar, 1988; Jüttner, 1994; Jüttner and others, 1995a, 1995b). Recreational boating on lakes and reservoirs using outboard marine engines introduces gasoline-related organic compounds including benzene, toluene, ethylbenzene, and xylenes to water bodies (Jüttner, 1988; van Donkelaar, 1988; Jüttner, 1994; Jüttner and others, 1995a, 1995b; Dale and others, 2000; Gabele and Pyle, 2000). Two-stroke outboard motors discharge a variety of compounds into the receiving water, with raw fuel being the most notable (Jackivicz and Kuzminski, 1973). Other possible sources of VOCs in lakes and reservoirs include accidental spills from fueling operations, leaking underground storage tanks in proximity to the lake or reservoir, leaking pipelines, stormwater runoff, atmospheric inputs, and fumigants from insecticide applications.

Purpose and Scope

The purpose of this report is to document LakeVOC, a deterministic model that can be used to estimate the level of VOC contamination in lakes and reservoirs. It is assumed that users of LakeVOC have knowledge of the processes influencing the transport and fate of organic compounds in lakes and reservoirs. A two-layer system is modeled on the basis of mixing between two water layers (epilimnion and hypolimnion) and volatilization and absorption to the atmosphere. LakeVOC model inputs include an initial concentration of the estimated VOC in the water body, wind speed, air temperature, atmospheric pressure, relative humidity, lake depth, lake depth/surface area

profile, epilimnion temperature, epilimnion depth, inflow and inflow depth, outflow and outflow depth, VOC inputs to the lake other than the atmosphere, atmospheric VOC concentrations, degradation rates in the epilimnion and hypolimnion, and diffusivity, solubility, and molecular weight of the VOC of interest.

This report describes the theoretical basis for the LakeVOC model, provides user instructions and information needs for using LakeVOC, and documents verification of the model using a hypothetical lake and an actual reservoir in southern California.

Acknowledgments

The authors thank Dr. James F. Pankow for the foresight and inspiration for the model, Melissa Dale and Richard Losee of the Metropolitan Water District of Southern California for providing the data for Lake Perris, California, Robert Broshears, Michael Majewski, James Pankow, and Lanna Combs for providing reviews of this report, and Ella Decker and Connie Ross for publication preparation.

DESCRIPTION AND THEORETICAL BASIS OF LakeVOC MODEL

General Description

LakeVOC represents a lake or reservoir as a two-layer system and estimates the concentration of an individual VOC in both the epilimnion (upper mixed layer) and hypolimnion (deep mixed layer). The model integrates the coupled system of differential equations for the concentration of the VOC in the epilimnion, the hypolimnion, the total mass of the VOC in the lake, volume of the epilimnion, and volume of the hypolimnion. LakeVOC accounts for changes in concentration caused by mixing, or exchange, between the two layers, direct addition of a VOC to the lake, loss of a VOC through lake outflows, air-water gas transfer of a VOC, and biochemical degradation. These processes are depicted schematically in figure 1.

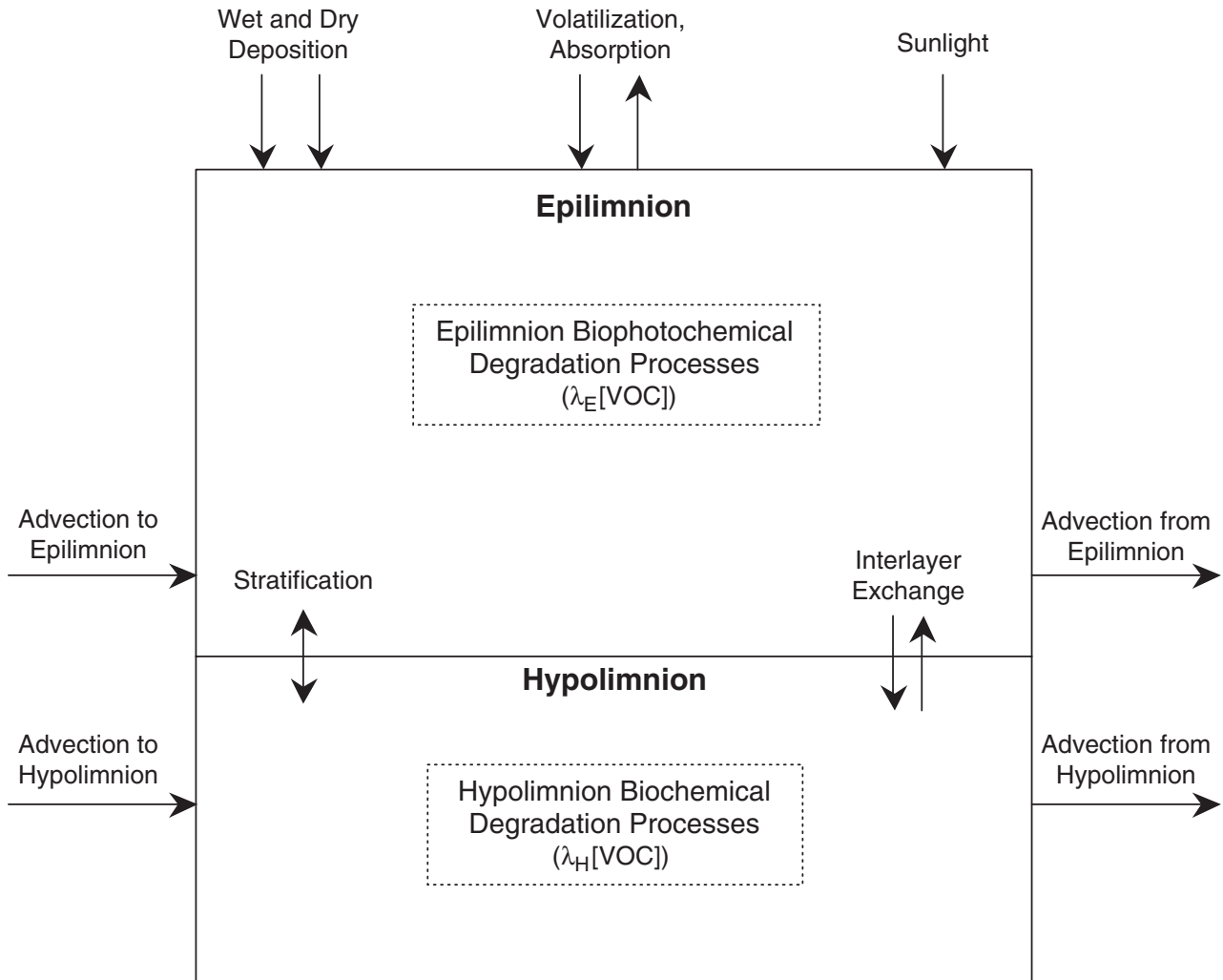


Figure 1. Schematic diagram showing the transport, behavior, and fate processes modeled by LakeVOC for volatile organic compounds in lakes and reservoirs.

The hydrodynamics of lake mixing and stratification are characterized in the model through user-entered time series for the depth of the mixed layer, lake depth, and lake inflows and outflows. The total lake volume is determined from the lake-depth time series and a separate user-entered profile of lake-surface area in relation to depth. Water is added to the lake by riverine inflow and (or) precipitation and a user-specified inflow volume. Water is removed from the lake by riverine outflow, evaporation, and a user-specified outflow volume. The depths of the user-specified inflows and outflows are independent and may be placed in either the epilimnion or hypolimnion.

Air-water gas transfer is characterized in terms of the air-water concentration difference and the wind speed using the relation of Wanninkhof and others (1991). Wind speed is entered by the user. Evaporation is characterized using the wind speed relation of Schwarzenbach and others (1993) assuming a relative humidity of 70 percent. The user-entered time-series data and physical constants for the model are described in detail in the following paragraphs. Parameters can be entered through a series of menus from the main program or through an ASCII parameter file. Numerical output from the model is displayed graphically and can be saved to an optional ASCII data file.

Air-Water Gas Transfer

The air-water flux of a VOC is characterized in LakeVOC in terms of the two-film model of air-water exchange. Detailed discussions of the two-film model are available elsewhere (Lewis and Whitman, 1924; Schwarzenbach and others, 1993; Rathbun, 1998), and only a brief discussion is given here. Although the two-film model oversimplifies the hydrodynamics associated with gas-liquid transfer, it provides a useful framework for estimating the rate of air-water exchange of VOCs.

The net flux, F , of a VOC across the air-water interface can be expressed in terms of a kinetic rate coefficient and a thermodynamic driving potential. The kinetic rate coefficient is referred to as the transfer velocity, and the driving potential is the air-water concentration difference. Therefore, F (mol/m²-s) is written as:

$$F = k_{OL}\Delta C, \quad (1)$$

where k_{OL} (m/s) is the liquid-side overall mass transfer velocity (Schwarzenbach and others, 1993; Rathbun, 1998) and ΔC (mol/m³) is the air-water concentration difference. The two-film model postulates that the magnitude of k_{OL} is determined by molecular diffusion through a thin stagnant layer of water and a stagnant layer of air at the air-water interface. The overall air-water transfer velocity, k_{OL} , can be calculated from the transfer velocities through these individual layers as:

$$\frac{1}{k_{OL}} = \frac{1}{k_L} + \frac{RT_W}{Hk_G}, \quad (2)$$

where k_L (m/s) is the transfer velocity through the water-side layer, k_G (m/s) is the transfer velocity through the air-side layer, R (m³-atm/K-mol) is the universal gas constant, T_W is the water temperature in degrees Kelvin (K), and H (atm-m³/mol) is the Henry's law coefficient.

The water-side transfer velocity, k_L , is calculated from the aqueous-phase molecular diffusivity, D_L (cm²/s), and wind speed at a height of 10 meters above the water surface for neutral atmospheric stability, U_{10} (m/s), using the relation of Wanninkhof and others (1991). This is:

$$k_L = 1.25 \times 10^{-6} \sqrt{\frac{600D_L}{\nu}} U_{10}^{1.64}, \quad (3)$$

where k_L is given in meters per second (m/s), ν is the kinematic viscosity of water in square centimeters per second (cm²/s) (for D_L in square centimeters per second), and U_{10} is in meters per second (m/s). Although the Wanninkhof and others (1991) relation is defined in terms of U_{10} , it is understood that for most applications of LakeVOC, values for U_{10} will not be available. In these cases, measurements of wind speed made at heights of other than 10 meters can be used without significant loss in accuracy of the model. Additionally, model performance will not be seriously impaired if these wind speeds are not corrected for changes in atmospheric stability. The air-side transfer velocity, k_G , is calculated from U_{10} at 20°C as (Schwarzenbach and others, 1993):

$$k_G = \left[\frac{D_G(\text{VOC})}{D_G(\text{H}_2\text{O})} \right]^{2/3} (0.0015 U_{10}), \quad (4)$$

where k_G is in meters per second and $D_G(\text{VOC})$ and $D_G(\text{H}_2\text{O})$ are the air-phase diffusivity of the VOC and water, respectively, in cm²/s. The ratio of the air-phase diffusivity can be expressed in terms of molecular weight, M_{VOC} (g/mol), and the air temperature, T_A (K), as (Atkins, 1986):

$$\frac{D_G(\text{VOC})}{D_G(\text{H}_2\text{O})} = \sqrt{\frac{18}{M_{\text{VOC}}}} \left(\frac{T_A}{293.16} \right)^{3/2}, \quad (5)$$

where the temperature term in equation 5 is necessary because equation 4 predicts k_G at a temperature of 20°C and the air temperature at a lake or reservoir could be substantially different.

The model calculates the aqueous-phase molecular diffusivity as a function of T_W using one of two formulae. The first method estimates D_L using the formula proposed by Wilke and Chang (1955) and the molar volume (V_M) at the normal boiling point of the VOC in cubic centimeters per mole (cm³/mol). Following Hayduk and Laudie (1974), D_L is then given by:

$$D_L = \frac{4.72 \times 10^{-7} T_W}{100 \mu V_M^{0.6}}, \quad (6)$$

in units of square centimeters per second (cm²/s) where T_W (K) is the water temperature and μ is the absolute viscosity of water in grams per centimeter per second [(g/cm)/s]. The second method calculates D_L using the polynomial expansions for the Schmidt number, Sc ($Sc = \nu/D_L$), from Wanninkhof (1992):

$$Sc = A + BT_W + CT_W^2 + DT_W^3, \quad (7)$$

where T_W in equation 7 is in degrees Celsius. Both μ and ν are calculated internally on the basis of T_W using freshwater data from Weast (1983). The user-entered parameter in equation 6 is V_M , and the user-entered parameters in equation 7 are A , B , C , and D . In general, it cannot be specified whether equation 6 or equation 7 is preferred for estimating D_L . That choice is made based on the VOC to be modeled and whether V_M or A , B , C , and D (or the diffusivity data required to calculate the four coefficients) are known.

Because the liquid-side transfer coefficient is used in the LakeVOC model, ΔC is expressed in terms of the VOC concentration in the epilimnion and the saturation concentration at the water surface, with the latter concentration predicted based on the atmospheric partial pressure of the VOC and its Henry's law coefficient, H . Using this information, equation 1 becomes:

$$F = k_{OL}(C_S - C_E), \quad (8)$$

where C_S (mol/m³) is the saturation concentration of the VOC, and C_E (mol/m³) is the concentration of the VOC in the epilimnion. The saturation concentration, C_S , is calculated from Henry's law and the Henry's law coefficient as:

$$C_S = \frac{P_A}{H}, \quad (9)$$

where P_A (atm) is the partial pressure of the VOC in the atmosphere and is computed as:

$$P_A = 1 \times 10^{-9} C_A P_{atm}, \quad (10)$$

where C_A is the atmospheric concentration of the VOC in parts per billion by volume (ppbv) (that is, the volume mixing fraction of the VOC in liters of VOC as a gas per liters of air) and P_{atm} is the total atmospheric pressure in atmospheres (atm).

Henry's law coefficients are calculated internally as a function of T_W using either the relation of Wanninkhof (1992) or that of Robbins and others (1993). The Wanninkhof relation is given by:

$$\ln(\alpha) = A_1 + A_2 \left(\frac{100}{T_W} \right) + A_3 \log \left(\frac{T_W}{100} \right) + S \left[B_1 + B_2 \left(\frac{T_W}{100} \right) + B_3 \left(\frac{T_W}{100} \right)^2 \right], \quad (11)$$

where α is the Ostwald solubility coefficient (Reid and others, 1987), S is salinity in parts per thousand (ppt) (for most applications of LakeVOC, S will likely be set to zero), and T_W is in degrees Kelvin (K). The Ostwald solubility can be converted to H using:

$$H = \frac{RT_W}{\alpha}. \quad (12)$$

The Robbins and others (1993) relation is given by:

$$H = \exp \left(A_0 - \frac{B_0}{T_W} \right), \quad (13)$$

for H in atmosphere-cubic meters per mole (atm-m³/mol) and T_W in degrees Kelvin (K). In equation 11, the user-entered parameters are A_1 , A_2 , A_3 , B_1 , B_2 , B_3 , and S , and in equation 13, the user-entered parameters are A_0 and B_0 . As in calculating D_L , the choice of whether equations 11 and 12 or equation 13 should be used to calculate H is left to the user, based on which set of coefficients are available for the VOC of interest.

Theoretical Formulation

The LakeVOC model solves the system of coupled differential equations for the VOC concentration in the epilimnion, C_E , the VOC concentration in the hypolimnion, C_H , the total mass of the VOC in the lake, M_T , the volume of the epilimnion, V_E , and the volume of the hypolimnion, V_H . In the general case, this system of equations is written as:

$$\frac{dV_E}{dt} = I_E - O_E + \Phi_{HE} - \Phi_{EH} + \delta - \varepsilon, \quad (14)$$

$$\frac{dV_H}{dt} = I_H - O_H - \Phi_{HE} + \Phi_{EH}, \quad (15)$$

$$\frac{dC_E}{dt} = \frac{[k_{OL}A_L(C_S - C_E) + M_{IN} + \Phi_{HE}C_H - \Phi_{EH}C_E + I_EC_S - O_EC_E + \delta_E]}{V_E} - \frac{C_E}{V_E} \frac{dV_E}{dt} - \lambda_EC_E, \quad (16)$$

$$\frac{dC_H}{dt} = \frac{[\Phi_{EH}C_E - \Phi_{HE}C_H - O_HC_H]}{V_H} - \frac{C_H}{V_H} \frac{dV_H}{dt} - \lambda_HC_H, \quad (17)$$

and

$$\frac{dM_T}{dt} = k_{OL}A_L(C_S - C_E) + M_{IN} + I_EC_S + \delta_E - O_EC_E - O_HC_H - \lambda_EC_E - \lambda_HC_H, \quad (18)$$

where I_E (m^3/day) is the inflow to the epilimnion, O_E (m^3/day) is the outflow from the epilimnion, Φ_{EH} (m^3/day) is the flow of water from the epilimnion to the hypolimnion, Φ_{HE} (m^3/day) is the flow of water from the hypolimnion to the epilimnion, δ (m^3/day) is the lake volume mass-balance term, ε (m^3/day) is the evaporation rate, I_H (m^3/day) is the inflow to the hypolimnion, O_H (m^3/day) is the outflow from the hypolimnion, A_L (m^2) is the lake-surface area, M_{IN} (mol/day) is the input of VOC from motorboats or other sources, δ_E (mol/day) is the epilimnion VOC mass balance term, and λ_E (mol/day) and λ_H (mol/day) are the biochemical degradation rates in the epilimnion and hypolimnion, respectively.

Conceptually, LakeVOC was designed to model managed lakes and reservoirs. With that in mind, the interpretation of the four terms I_E , O_E , I_H , and O_H are the inflows and outflows that can be set by the operator. Physically, they could be open channel flow, flow rates through pipelines, floodgates, or power turbines. However, it is recognized that these may not be the only

inflows or outflows to a lake or reservoir. Following this, it is possible that changes in the total lake volume (as set by the user-entered changes in lake depth) may not balance changes in volume calculated using I_E , O_E , I_H , and O_H . Therefore, an additional lake inflow/outflow term is required to ensure balance of water flow in the lake or reservoir. Physically, δ represents this net volume of water added or removed from the lake by precipitation or rivers not accounted for by I_E , O_E , I_H , and O_H . Because δ can be positive (water added) or negative (water removed), the epilimnion VOC mass-balance term, δ_E , in equation 16 represents the mass of the VOC gained or lost by the epilimnion through the make-up flow defined by δ . Correspondingly δ_E is defined as:

$$\delta_E = \delta C_S \quad \delta > 0,$$

or

$$\delta_E = \delta C_E \quad \delta < 0. \quad (19)$$

VOC concentrations in inflows to the epilimnion are assumed to be in atmospheric equilibrium. VOC concentrations in inflows to the hypolimnion are assumed to be zero. It should be noted that the purpose of LakeVOC is to assist lake and reservoir operators in managing the use of watercraft. Restriction of LakeVOC to studying cases where VOC input is distributed over the surface of a lake (as in the case of use of recreational watercraft) is the reason for limiting inflow VOC concentrations to be that of C_S .

The inflows and outflows, I_E , I_H , O_E , and O_H , and the interlayer exchange terms, Φ_{EH} and Φ_{HE} , in equations 14-18 are specified from the user-entered time series for total lake depth, depth of the mixed-layer, lake inflow, lake outflow, and the heights of inflows and outflows relative to the lake bottom. In calculating the exchange terms and inflows and outflows, the model uses only one user-defined inflow and one user-defined outflow to calculate I_E , I_H , O_E , and O_H . Although the inflow and outflow can be positioned independently, once these depths are set, one of the inflows must be zero and one of the outflows must be zero (the model cannot have two inflows or two outflows). Furthermore, the model also can assume that either $\Phi_{EH}=0$, $\Phi_{HE}=0$, or $\Phi_{EH}=\Phi_{HE}=0$ (water moves only one way or not at all across the thermocline) and that Φ_{EH} and Φ_{HE} can be replaced by a general exchange term Φ which is positive for flow from the epilimnion to the hypolimnion. The user specifies dV_T/dt , dV_E/dt , dV_H/dt , and one of the following pairs of inflows and outflows: (I_E , O_E); (I_E , O_H); (I_H , O_E); or (I_H , O_H). The model then calculates evaporation rate, ε , using:

$$\varepsilon = A_L k_G(H_2O) \frac{V_P}{RT_W} (1 - R_H), \quad (20)$$

where A_L is the lake-surface area, $k_G(H_2O)$ is the gas-side transfer velocity for water, R_H is the relative humidity, and V_P is the vapor pressure of water. R_H is user defined, V_P is estimated from T_W using the data of Weast (1983), and $k_G(H_2O)$ is calculated from U_{10} and T_A using equation 4. The model then determines Φ by rearranging equation 15 to give:

$$\Phi = \frac{dV_H}{dt} - I_H + O_H, \quad (21)$$

where equation 21 is the general form and it is understood that either or both I_H and O_H may be zero. With Φ known, δ can be calculated from equation 14.

On basis of the input data, some of the inflow, outflow, or exchange terms may be equal to zero, in which case equations 14-18 simplify from the general case. For example, when both the lake inflow and outflow are in the epilimnion, the total volume of the lake, V_T , is increasing, $dV_T/dt=dV_E/dt$, and $dV_H/dt=0$, then the model assumes that $I_H=0$ and $O_H=0$. Under these conditions, $\delta=0$ and $\Phi=0$ and equations 14-18 simplify to

$$\frac{dV_E}{dt} = I_E + \delta, \quad (22)$$

$$\frac{dV_H}{dt} = 0, \quad (23)$$

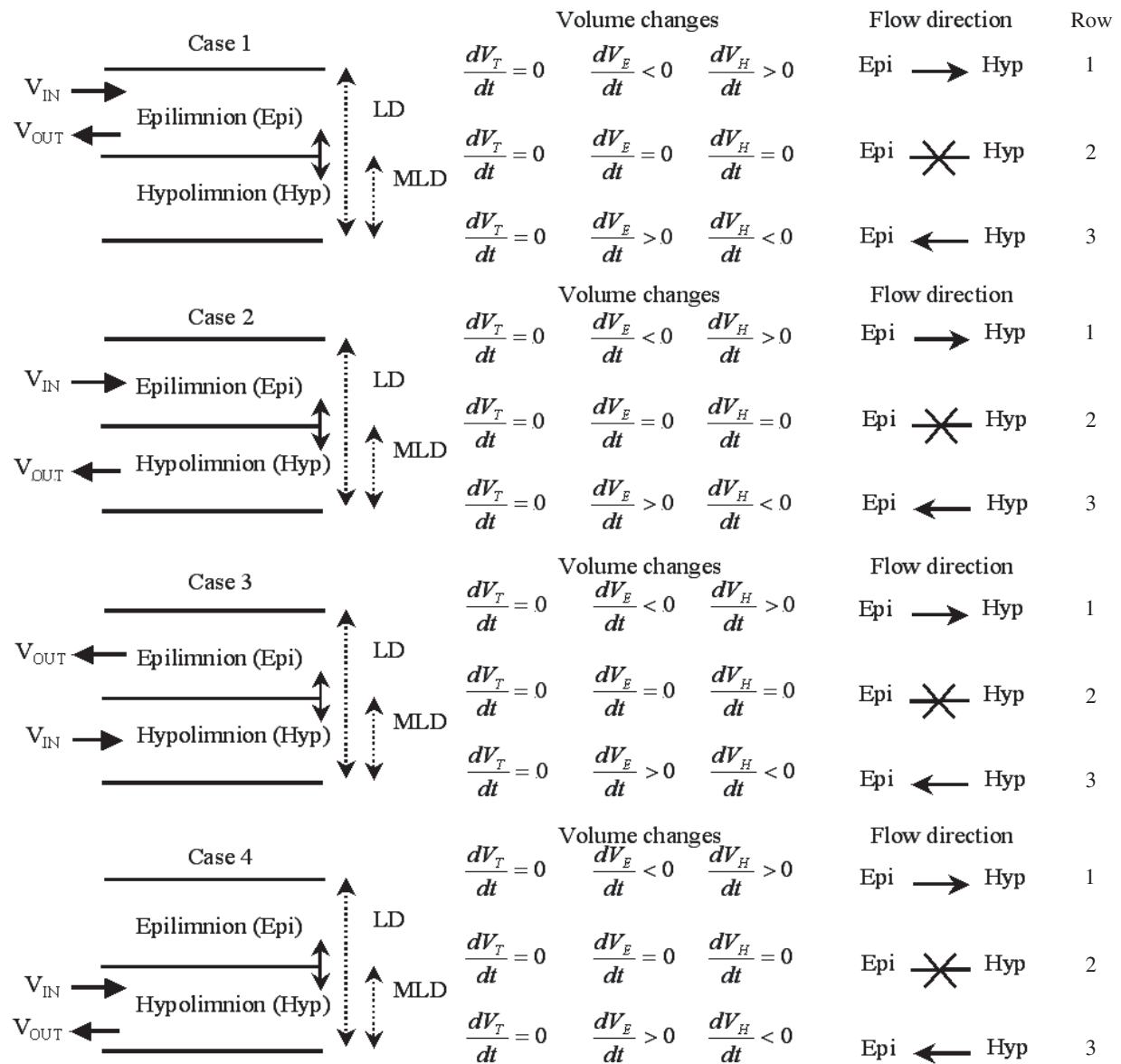
$$\frac{dC_E}{dt} = \frac{[k_{OL}A_L(C_S - C_E) + M_{IN} + I_E C_S + \delta C_S]}{V_E} - \frac{C_E}{V_E} \frac{dV_E}{dt} - \lambda_E C_E, \quad (24)$$

$$\frac{dC_H}{dt} = -\lambda_H C_H, \quad (25)$$

and

$$\begin{aligned} \frac{dM_T}{dt} &= k_{OL}A_L(C_S - C_E) + M_{IN} \\ &+ I_E C_S + \delta C_S - \lambda_E C_E - \lambda_H C_H. \end{aligned} \quad (26)$$

Situations that are more complicated arise when lake inflows and outflows are in different layers or when there is exchange of water between the epilimnion and hypolimnion. Figure 2 illustrates the different cases for mixing and volume changes as characterized in the model. The complete set of equations used in the LakeVOC model as derived from the lake-mixing scenarios shown in figure 2 are listed in the subroutine CONCFUNC.F90, which is included as part of Appendix A.



EXPLANATION

- LD LAKE DEPTH
- MLD MIXED LAYER DEPTH
- Epi EPILIMNION
- Hyp HYPOLIMNION

Figure 2. Schematic diagram of different lake-mixing scenarios in LakeVOC model and implied water transfer between the epilimnion and hypolimnion. The volume changes are read into the model across a row for a given location of the inflow and outflow (defined by the location of the **bold** arrows associated with V_{IN} and V_{OUT}). For example, for inflows and outflows situated as shown in case 3, volume changes such as shown in row 3 imply a net flow of water from the hypolimnion to the epilimnion.

The volumes V_E , V_H , and V_T , all in cubic meters (m^3), are calculated from the total lake depth, D_T (m), and epilimnion depth, D_E (m), using a user-specified profile of lake-surface area as a function of depth. An example of a profile of lake-surface area in relation to lake depth is plotted in figure 3. The lake surface is assumed to be circular so that the volume of any layer can be calculated as the sum of cylindrical and conic sections, depending on the shape of the surface area in relation to the depth profile. The volume of a cylindrical layer is calculated as the surface area multiplied by the layer thickness. The volume of a conical layer, $V_{L,i}$ (m^3) is calculated from:

$$V_{L,i} = \frac{\pi h}{3}(r_1^2 + r_1 r_2 + r_2^2), \quad (27)$$

where h (m) is the thickness of the layer, and r_1 (m) and r_2 (m) are the radii of the top and bottom layers, respectively. The layer radii, r_1 and r_2 , are calculated from the respective lake areas at those depths using the relation:

$$r_N = \sqrt{\frac{A_L(z_N)}{\pi}}, \quad (28)$$

where N equals 1 or 2 and $A_L(z_N)$ is the area of the lake at depth, z_N , as entered in the lake area in relation to the depth profile. Therefore, V_E and V_H are calculated as the sum of the individual layers as:

$$V_E = \sum_{i=1}^{N_E} V_{L,i},$$

and

$$V_H = \sum_{i=1}^{N_H} V_{L,i}, \quad (29)$$

where N_E and N_H are the number of layers in the epilimnion and hypolimnion, respectively. Note that the layers used to calculate V_E and V_H are determined solely from the lake area in relation to the depth profile.

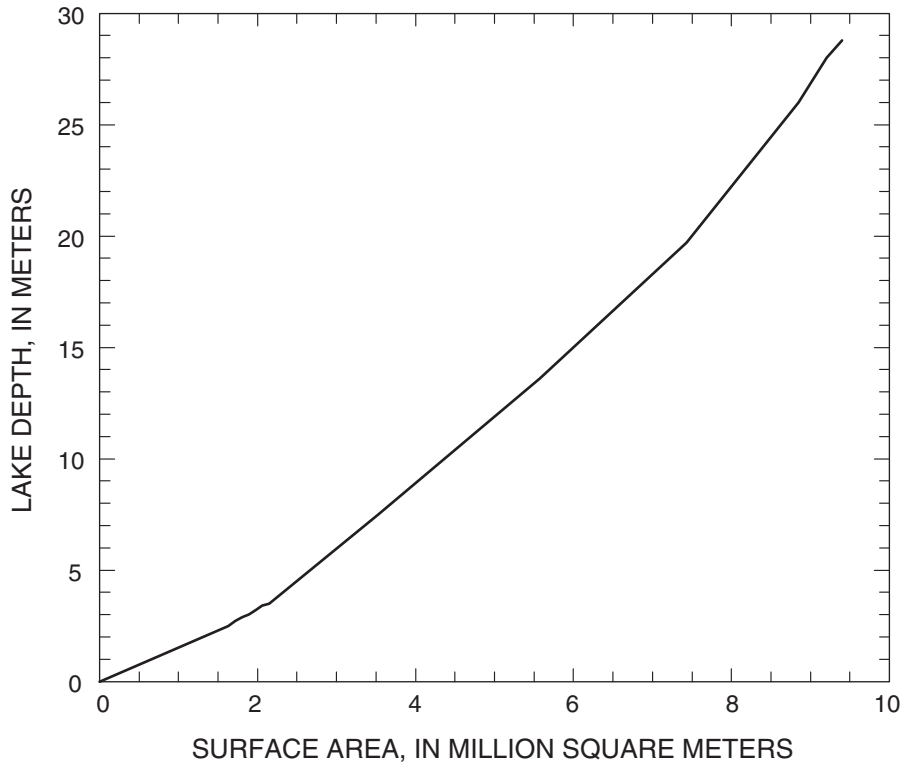


Figure 3. Lake profile of lake depth in relation to surface area.

Model Operation and Numerical Methods

Table 1 lists the user-entered data needed for the LakeVOC model and denotes if a time series or a constant is required. Each time series may be entered as a monthly, weekly, or daily time series with 12, 52, or 365 data points, respectively. Table 2 lists time series of parameters and constants derived by the model from some of the input listed in table 1. All of the needed derived time series are calculated as daily time series. Because there is no provision for entering more than 1 year of data, the model assumes that each time series represents each year for multiyear simulations. Before the differential equations can be integrated, a new time series entered as monthly or weekly values are converted to a daily time series by linear interpolation. These daily time series then are used as “look-up tables” to provide the physico-chemical, hydrological, and meteorological parameters for using the model.

The lake volumes V_E and V_H are calculated from the time series for lake depth and mixed-layer depth. The changes in these volumes are then used to compute the derivatives dV_E/dt and dV_H/dt . The user enters a single time series for lake inflow and a single time series for lake outflow. The model combines these data with the inflow and outflow height data and the position of the thermocline to calculate the independent time series for I_E , I_H , O_E , and O_H noting that when $I_E \neq 0$, $I_H = 0$ (and vice versa) and when $O_H \neq 0$, $O_E = 0$ (and vice versa).

The set of differential equations is integrated using a variable-step-size Runge-Kutta routine (Press and others, 1992). In particular, LakeVOC uses the Numerical Algorithms Group routine D02BBF (The Numerical Algorithms Group, FORTRAN Library Mk 18 for Compaq Visual Fortran, Oxford, England). This particular subroutine has the option of saving intermediate data points to a file and displaying them on the screen. For each step taken by the Runge-Kutta, the model calculates k_{OL} , C_S , ϵ , F , and δ and uses the values to solve the relevant form of equations 14-18.

USER INSTRUCTIONS AND INFORMATION NEEDS FOR LakeVOC MODEL

Using LakeVOC Model

LakeVOC has been tested under all 32-bit versions of Microsoft Windows operating system through

Windows XP (Home and Professional). LakeVOC can be installed using a shortcut from the desktop in all 32-bit versions of Microsoft Windows operating systems, double clicking on the file LakeVOC.exe in Windows Explorer, or from the "Start button Program/Run" menu.

Parameters to use the model are entered through a series of dialog menus found under the “Setup” menu in the main window. A list of user-defined parameters and the units LakeVOC expects as input are listed in table 1. The specific setup menu where these parameters may be located is listed in table 3. The user is notified if LakeVOC detects an incorrect variable or inconsistency in the input data. In most cases, LakeVOC will not start with incorrect data. However, it is possible to cause either model failure or program termination by specifying conditions or parameters that cause numerical instability or floating-point errors. For this reason, it is wise to save all modifications to parameters before starting the model.

Parameters also can be entered through an ASCII parameter file with the default extension of “.PAR.” Details of the structure of a valid parameter file can be found by first writing a copy of the default parameters to a file. In general, the first character of the title line preceding the data for each time series must be a “1,” a “2,” or a “3.” If the first character is a 1, the program will expect the following time series to contain the 12 values for the monthly data, with the first element corresponding to the data for January. If the first character is a 2 or 3, then the model will expect the following line to contain the filename of the data file holding the weekly or daily data, respectively. The filename can include a directory path, provided the filename and directory path are separated by the string “\$\$\$” as shown in the following example:

```
c:\lakevoc\datafile\$$$data.dat
```

The data files for the daily or weekly data should be ASCII files and have the following format shown for daily data with a tab between the day or week and data values:

Day	DataValue
1	25.6
2	25.8
...	
365	25.7

Table 1. User-entered data needed for LakeVOC model

[VOC, volatile organic compound; kg/mo, kilogram per month; kg/wk, kilogram per week; kg/d, kilogram per day; ppbv, parts per billion by volume; K, degrees Kelvin; °C, degrees Celsius; m/s, meters per second; atm, atmospheres; %, percent; m³/mo, cubic meters per month; m³/wk, cubic meters per week; m³/d, cubic meters per day; µg/L, micrograms per liter; g/mol, grams per mole; mL/mol, milliliters per mole; m², square meters]

Data description	Symbol	Equation	Data type	Units of measurement
VOC input from motorboats or other sources	M_{IN}	(16, 18, 24, 26)	Time Series	kg/mo, kg/wk, kg/d
Atmospheric VOC concentrations	C_A	(10)	Time Series	ppbv
Epilimnion degradation rate	λ_E	(16, 18, 24, 26)	Time Series	day ⁻¹
Hypolimnion degradation rate	λ_H	(17, 18, 25, 26)	Time Series	day ⁻¹
Air temperature	T_A	(5)	Time Series	K
Wind speed	U_{10}	(3, 4)	Time Series	m/s
Atmospheric pressure	P_{atm}	(10)	Time Series	atm
Relative humidity	R_H	(20)	Constant	%
Lake depth	D_T		Time Series	meters
Epilimnion depth	D_E		Time Series	meters
Epilimnion temperature	T_W	(2, 6, 7, 11, 12, 13, 20)	Time Series	°C
Lake inflow volume	L_I		Time Series	m ³ /mo, m ³ /wk, m ³ /d
Lake outflow volume	L_O		Time Series	m ³ /mo, m ³ /wk, m ³ /d
Inflow height	H_I		Time Series	meters
Outflow height	H_O		Time Series	meters
Initial VOC concentration	C_0		Constant	µg/L
VOC molecular weight	M_{VOC}	(5)	Constant	g/mol
VOC molar volume	V_M	(6)	Constant	cm ³ /mol
Wanninkhof (1992) coefficients for Schmidt number, Sc	$A,$ $B,$ $C,$ D	(7)	Constants	dimensionless, °C ⁻¹ , °C ⁻² , °C ⁻³
Robbins and others (1993) coefficients for Henry's law constant, H	$A_0,$ B_0	(13)	Constants	dimensionless, °C
Wanninkhof (1992) coefficients for Henry's law constant, H	$A_1,$ $A_2,$ $A_3,$ $B_1,$ $B_2,$ B_3	(11)	Constants	dimensionless, °C, dimensionless, dimensionless, °C ⁻¹ , °C ⁻²
Salinity	S	(11)	Constant	parts per thousand (ppt)
Lake-surface area in relation to depth profile	$A_L(z)$	(28)	Array	m ² and meters
Points in $A_L(z)$	N_A		Constant	dimensionless
Total simulation time	T_S		Constant	years
Data output time step	T_O		Constant	days
Runge-Kutta tolerance	ε_T		Constant	dimensionless

Table 2. Time series and constants derived from the user-entered time series in LakeVOC model

[VOC, volatile organic compound]

Data description	Symbol	Data type	Equation	Derived from:
Overall transfer velocity	k_{OL}	Time Series	(2)	U_{10}, T_A, T_W
Water-side transfer velocity	k_L	Time Series	(3)	ν, U_{10}, D_L
Air-side transfer velocity	k_G	Time Series	(4)	$\frac{D_G(VOC)}{D_G(H_2O)}, U_{10}$
Air-phase diffusivity of the VOC divided by the diffusivity of water	$\frac{D_G(VOC)}{D_G(H_2O)}$	Time Series	(5)	M_{VOC}, T_A
Aqueous-phase molecular diffusivity	D_L	Time Series	(6)	T_W, μ, V_M
Aqueous-phase molecular diffusivity	D_L	Time Series	text p. 5	Sc, ν
Schmidt number	Sc	Time Series	(7)	A, B, C, D, T_W
Net Flux	F	Time Series	(8)	k_{OL}, C_S, C_E
Saturation concentration	C_S	Time Series	(9)	P_A, T_W
Partial pressure of the VOC	P_A	Time Series	(10)	C_A, P_{atm}
Ostwald solubility	α	Time Series	(11)	$A_1, A_2, A_3, B_1, B_2, B_3, T_W, S$
Henry's law constant	H	Time Series	(12)	R, T_W, α
Henry's law constant	H	Time Series	(13)	A_0, B_0, T_W
Lake volume mass balance term	δ	Time Series	(14)	$D_E, D_T, I_E, I_H, O_E, O_H$
Epilimnion VOC mass-balance term	δ_E	Time Series	(19)	C_E or C_S, δ
Evaporation rate	ε	Time Series	(20)	$U_{10}, T_A, T_W, A_L, M_{VOC}, V_P, R, R_H$
Interlayer exchange term	Φ	Time Series	(21)	$D_E, D_T, I_E, I_H, O_E, O_H$
Epilimnion volume	V_E	Time Series	(29)	$D_E, D_T, A_L(z)$
Hypolimnion volume	V_H	Time Series	(29)	$D_E, D_T, A_L(z)$

Table 3. Menu structure and location of model parameters

[VOC, volatile organic compound]

Setup menu	Variable	Submenus	Variable	Data type
VOC parameters	M_{VOC}			Constant
	C_0			Constant
		VOC inputs	M_{IN}	Time series
		Atmospheric VOC concentrations	P_A	Time series
		Epilimnion degradation rate	λ_E	Time series
		Hypolimnion degradation rate	λ_H	Time series
		Solubility characterization		
			A_0	Constant
			B_0	Constant
			A_1	Constant
			A_2	Constant
			A_3	Constant
			B_1	Constant
			B_2	Constant
			B_3	Constant
			S	Constant
		Diffusivity characterization		
			V_M	Constant
			A	Constant
			B	Constant
		C	Constant	
		D	Constant	
Meteorological parameters		Atmospheric pressure	P_{atm}	Time Series
		Wind speed	U_{10}	Time Series
		Air temperature	T_A	Time Series
		Relative humidity	R_H	Constant
Hydrological parameters	N_A			Constant
		Lake depth	D_T	Time Series
		Mixed-layer depth	D_E	Time Series
		Mixed-layer temperature	T_W	Time Series
		Inflow volume	L_I	Time Series
		Outflow volume	L_O	Time Series
		Inflow height	H_I	Time Series
		Outflow height	H_O	Time Series
		Lake-area profile	$A_L(z)$	Array
Time parameters	T_S			Constant
	T_O			Constant
	ε_T			Constant
	Run Title			String
	Comment 1			String
	Comment 2			String

Variables in the parameter file can be edited using any ASCII editor such as NOTEPAD™ or a programming editor (for example, UltraEdit, Kedit, Zeus, or Epsilon). In general, word processors should not be used to edit parameter files because of embedded control characters. As in the case of manual entry of parameters through the dialog menus, the user will be notified of inconsistencies and errors in the parameter file when it is read into LakeVOC.

After the input parameters have been set, the model is started by the “Start Model” option under the “Run” menu in the main window. Model output to the main screen should begin soon after the model has been started. While the model is running, the input parameters generally cannot be modified. The user may terminate model use before the final time value using the “Stop Model” option in the “Run” menu. The model also may be paused during a simulation using the “Pause Model” option. This allows the user to modify the VOC lake inputs (M_{IN}) and atmospheric VOC concentrations (C_A). These are the only two time series that may be modified when the model is paused.

Data output from the model may be saved to disk at a fixed time interval that is set in the “Runtime Parameters” dialog menu. The default output time step is 1 day. Users are limited to 10,000 total output points per model simulation. The drive, directory, and file that the data are written to is set by the “Save VOC Results” option under the “File” menu in the main window. A new data file is opened by the user for each model simulation. If the model is initiated without an output filename specified, the user will be notified that the results will not be saved to disk.

Example physical/chemical input parameters for MTBE and other selected VOCs are provided in Appendix D.

Known Problems or Cautions in Using the LakeVOC Model

There are four known problems or cautions in using the LakeVOC model. These problems or cautions are: (1) all initial inputs cannot be set to zero; (2) a problem with a display of the input/output (I/O) menu files; (3) the output time step is independent of the step size in the Runge-Kutta solution; and (4) the model should be used with several different tolerance values to assure that erroneous results are not produced. The four known problems or cautions are described in more detail in the following paragraphs.

1. The Runge-Kutta routine used is an adaptive step-size algorithm. Therefore, there must be some change in the dependent variables before it can initialize and start integrating. Operationally, this means that all of the initial inputs cannot be set to zero or the model started with the system in equilibrium. For instance, attempts to start the model with an initial VOC concentration of zero, an atmospheric concentration of zero, a VOC input of zero, and a wind speed of zero will cause the Runge-Kutta routine to fail. This problem can be avoided by setting any of the initial inputs to a small value (for example, setting the atmospheric concentration to 0.01 ppbv will allow the model to start).
2. The file I/O menus do not display the files in the current working directory as the default when the menu is opened. If the default extension is typed into the “filename” entry, a listing of files in the directory will be displayed correctly. For example, if the “Read Parameter File” menu is invoked, the program should display a list of files with extension “.PAR” in the current directory. However, under Windows 95 and NT 4.0 the window will be blank. Entering “*.par” in the filename space in the menu box will cause all of the parameter files to be listed correctly.
3. The output time step parameter is independent of the step size taken by the Runge-Kutta routine. In most cases, an output time step of 1 day will provide adequate temporal resolution in the ASCII output. If the user needs more accuracy in the calculation or if the model is becoming numerically unstable, the tolerance parameter can be decreased. However, computation time of the model increases nonlinearly with decreases in tolerance.
4. It is prudent to provide a simulation with several different values of the tolerance parameter. Like all numerical solutions of differential equations, the model can produce erroneous results if used with too high a tolerance. It is suggested that the tolerance be decreased until there is little change in the model output. This is especially true if the simulation has long periods (for example, several days or longer) during which conditions do not change. In these instances, the Runge-Kutta routine may take a large time step and step over a transition. A good example of this result can be found in the dilution tests listed in table 4. Some of these tests can give negative values for concentrations when the inflows and outflows are initializing if too high a value for tolerance is used.

Table 4. Model verification simulations, conditions, and results

[M_{IN} , VOC inputs from motorboats or other sources; kg, kilograms; D_E , depth of epilimnion; m, meters; H_I , inflow height above bottom; H_O , outflow height above bottom; L_I , lake inflow volume; L_O , lake outflow volume; m³/d, cubic meters per day; U_{10} , wind speed at 10 meters above water surface; m/s, meters per second; VOC, volatile organic compound; [VOC], volatile organic compound concentration; mg/L, milligrams per liter; ppbv, parts per billion by volume; E, epilimnion; H, hypolimnion]

Simulation number	Purpose	M_{IN} (kg)	D_E (m)	H_I / H_O L_I / L_O (m ³ /d)	U_{10} (m/s)	Atmospheric concentration [VOC] (ppbv)	Calculated analytical concentration [VOC] (mg/L)	Model estimated concentration [VOC] (mg/L)
1	Test addition of VOC for conservation of mass	100	50	10/10 0/0	0	0	1.000	0.999
2	Test dilution of VOC with no interlayer exchange	100	50	10/10 100/100	0	0	.941	.941
3	Test dilution of VOC with stratification, no interlayer exchange	100	25	10/10 100/100	0	0	1.770	1.771
4	Test of VOC dilution with stratification and interlayer exchange, inflow to hypolimnion, outflow from epilimnion	100	25	10/48 100/100	0	0	1.770	1.771
5	Test of VOC dilution with stratification and interlayer exchange, inflow to epilimnion, outflow from hypolimnion	100	25	48/10 100/100	0	1,000	(E) 1.829	(E) 1.829
6	Test of VOC dilution in hypolimnion with interlayer exchange and varying lake depth, inflow to hypolimnion, outflow from hypolimnion	100	25	10/10 (H)328.8	0	0	(H) .358	(H) .358
7	Test of lake equilibration with stratification and interlayer exchange, inflow to epilimnion, outflow from hypolimnion	100	25	48/10 2000/2000	0	1,000	(E) .510 (H) .510	(E) .510 (H) .512
8	Test of gas exchange, unstratified lake	100	50	10/10 0/0	¹ 5	0	.599	.599
9	Test of gas exchange, unstratified lake, equilibration test	100	50	10/10 0/0	² 10	1,000	.510	.512

¹ $U_{10} = 5$ m/s for period April through July, $U_{10} = 0$ m/s at all other times.

² $U_{10} = 10$ m/s for period April through December, $U_{10} = 0$ m/s at all other times.

VERIFICATION OF LakeVOC MODEL

The LakeVOC model was verified in a series of 11 simulations. The first nine simulations used a hypothetical lake, and simulations 10 and 11 used an actual water-supply reservoir. The first seven simulations verified lake mixing and dilution, and simulations 8 and 9 verified the gas exchange between the atmosphere and the lake. Simulations 10 and 11 were used to verify the LakeVOC model with actual environmental conditions in a reservoir. Simulation 10 verified the model's ability to estimate dissolved oxygen concentrations and lake volumes. Simulation 11 verified the model's ability to estimate MTBE concentrations from daily, weekly, and monthly model input parameters.

Simulations Using a Hypothetical Lake

The LakeVOC model was verified, in part, by using a series of controlled simulations designed to test model characterizations of conservation of mass, air-water gas exchange, mixing between the epilimnion and hypolimnion, evaporation, and volume changes due to inflow and outflow. Seven simulations were conducted to test the model characterizations of VOC addition, mixing, and lake inflows and outflows. Two additional simulations were conducted to test the model characterization of air-water gas exchange. The conditions for the nine simulations using a hypothetical lake are summarized in table 4. Validation simulations were conducted using a hypothetical lake with a surface area of 2,000 m², a depth of 50 m, T_W and T_A equal to 10°C, and $R_H = 100$ percent. The VOC selected for these hypothetical lake simulations was MTBE. Input time series were given as monthly averages.

Lake Mixing and Dilution Tests

Simulations 1-7 were designed to test the model characterization of mixing, exchange of water between the epilimnion and hypolimnion, and addition or removal of water from the lake. Mass balance of the VOC was simplified by setting $U_{10} = 0$ m/s so that gas exchange was shut off for the entire year. In summary, no anomalous results were found for any of the dilution test cases described in detail in the following paragraphs. This demonstrated that the characterization of mixing and dilution just described was implemented correctly in the LakeVOC model. Appendix B presents the input parameter files for these simulations.

Simulation 1: This simulation verified that the hypothetical lake conserved the mass of VOC under equilibrium conditions. In February, 100 kg of MTBE were added to the unstratified lake. In this case, the calculated analytical concentration of MTBE in the lake, calculated on the basis of volume, was 1.000 mg/L. The model estimated a concentration of 0.999 mg/L.

Simulation 2: This simulation verified that the model correctly characterized dilution when water was added and removed from the lake by surface inflows and outflows with no interlayer exchange. Atmospheric concentrations of MTBE were set equal to zero so that the inflow to the lake contained no MTBE. In February, 100 kg of MTBE were added to the unstratified lake, resulting in an initial MTBE concentration of 0.999 mg/L. The lake remained unstratified throughout the year, and there was a 100 m³/d inflow and outflow in May and June. The inflow of water did not contain MTBE, thus the lake was diluted. The calculated analytical concentration after dilution and the model-estimated concentration in the lake were 0.941 mg/L.

Simulation 3: This simulation verified that a stratified lake with an inflow and outflow in the epilimnion correctly characterized dilution with no interlayer exchange. The lake thermocline was set at a depth of 25 m. As in simulation 2, atmospheric MTBE concentrations were set equal to 0, and 100 kg of MTBE were added to the lake in February, resulting in an initial MTBE concentration in the epilimnion of 1.999 mg/L. In May and June, there was a 100 m³/d inflow to and outflow from the epilimnion. The calculated analytical concentration in the lake based on this dilution was 1.770 mg/L. The model estimated an MTBE concentration of 1.771 mg/L, which closely matched the calculated analytical concentration.

Simulation 4: The conditions for this simulation were identical to simulation 3 except that the inflow was in the hypolimnion instead of the epilimnion. This caused a flow from the hypolimnion to the epilimnion (interlayer exchange) with the net effect on MTBE concentrations identical to simulation 3. In this case, the water added to the hypolimnion had no MTBE so the dilution was identical to simulation 3. The calculated analytical MTBE concentration in the lake was 1.770 mg/L, and the model estimate was 1.771 mg/L.

Simulation 5: In this simulation, the inflow was in the epilimnion and outflow was in the hypolimnion of the lake, as in simulation 3. However, the atmospheric MTBE concentration was set at 1,000 ppbv. Although this air-phase concentration is unrealistically

high, it was used so that the surface-water inflow to the lake would have a high enough MTBE concentration to make a large difference in the overall lake concentrations. Similar to the previous simulations, 100 kg of MTBE were added to the lake in February, resulting in an initial concentration in the epilimnion of 2 mg/L. In May and June, there was a $100 \text{ m}^3/\text{d}$ inflow to the epilimnion with a $100 \text{ m}^3/\text{d}$ outflow from the hypolimnion. The net result of this flow was to dilute the epilimnion with water having MTBE concentrations in equilibrium with the atmosphere. The closed-form analytical solution of the dilution equation showed that the MTBE concentration in the epilimnion was 1.829 mg/L, which was identical to the model-estimated concentration. MTBE was added to the hypolimnion by interlayer transfer, but it was not possible to obtain a closed-form analytical solution for the concentration equation in the hypolimnion.

Simulation 6: This simulation tested dilution in the hypolimnion by allowing lake depth and epilimnion thickness to decrease while keeping hypolimnion volume constant. The lake outflow was from the hypolimnion, so decreases in lake depth under these conditions would move water from the epilimnion to the hypolimnion, then through the outflow. Keeping the epilimnion concentration constant by setting $U_{10} = 0 \text{ m/s}$ allowed a closed-form analytical solution for the hypolimnion concentration equation. In simulation 6, $U_{10} = 0 \text{ m/s}$, $R_H = 100$ percent, the atmospheric MTBE concentration was equal to zero, and 100 kg of MTBE were added to the epilimnion in February. An outflow flow rate of $328.8 \text{ m}^3/\text{d}$ was applied to the hypolimnion for the month March. This resulted in the epilimnion volume decreasing from 5.0×10^4 to $4.0 \times 10^4 \text{ m}^3$. The calculated analytical concentration for the increase in the hypolimnion concentration was 0.358 mg/L, and the model-estimated concentration was 0.358 mg/L.

Simulation 7: The final dilution simulation verified that the lake would attain a stable equilibrium concentration with a large inflow and outflow. The inflow was set in the epilimnion, and the outflow set in the hypolimnion. Inflow and outflow rates were $2 \times 10^3 \text{ m}^3/\text{d}$ throughout the time period from May to November. Atmospheric MTBE concentrations were set at 1,000 ppbv throughout this same time period. Because the inflow was in the epilimnion, the incoming water was assumed to have an MTBE concentration equal to C_S , or 0.510 mg/L. Given the high flow rates and the mixing pattern for the specified conditions in this simulation, the entire lake would be expected to reach this concentration. The MTBE concentrations

estimated by the LakeVOC model under these conditions were 0.510 mg/L in the epilimnion and 0.512 mg/L in the hypolimnion.

Gas-Exchange Tests

Simulations 8 and 9 were designed to test the model characterization of air-water exchange. Mass balance of the VOC was simplified by setting the atmospheric MTBE concentration to zero, assuming there were no inflows or outflows, and using an unstratified lake. In summary, the two simulations described in the following paragraphs showed that the characterization of the air-water gas exchange just described was correctly represented by the LakeVOC model. See Appendix B for the input parameter files for these simulations.

Simulation 8: This simulation tested the air-water gas flux of MTBE estimated by the LakeVOC model. The model flux was determined as the time rate of change of the concentration of MTBE for a constant wind speed. Aqueous-phase concentrations of MTBE were elevated above saturation by adding 100 kg of MTBE into the unstratified lake in February. A constant $U_{10} = 5 \text{ m/s}$ from April to July was used as the driving force for gas exchange. An analytical solution for the MTBE concentration was obtained for the month of June under these conditions. The model estimated an MTBE concentration of 0.599 mg/L in the lake, which was equal to the calculated analytical concentration.

Simulation 9: This simulation tested whether the lake would come to equilibrium with respect to the atmospheric MTBE concentration. In February, 100 kg of MTBE were added to the lake with $U_{10} = 10 \text{ m/s}$ from April through November. The atmospheric concentration of MTBE was set at 1,000 ppbv, which corresponded to an aqueous-phase MTBE concentration of 0.510 mg/L at $T_W = 10^\circ\text{C}$. At the end of November, the model estimated an MTBE concentration of 0.512 mg/L in the lake, which was in good agreement with the calculated analytical concentration.

Simulations Using an Actual Reservoir

Simulations using an actual water-supply reservoir, Lake Perris, located in Riverside County, California, with water-quality data provided by the

Metropolitan Water District of Southern California (MWDSC) (1999), were used to further verify results from the LakeVOC model. Two simulations were done (simulations 10 and 11) to assess model accuracy in estimating: (1) the depths and volumes of the epilimnion and hypolimnion, and (2) the measured concentrations of a VOC with daily, weekly, and monthly hydrographic, meteorologic, and VOC input parameters. Dissolved oxygen (DO) measurements and a first-order degradation rate of DO in the hypolimnion were used to calibrate the hydrodynamics of the LakeVOC model for Lake Perris, whereas boating usage and estimated mass emission rates from marine engines were used to calibrate the model to estimate the concentration of a VOC in the reservoir. Calibration of the MTBE concentrations in Lake Perris was performed on 1.5 years of data and verified with a different, but similar, period of data.

Lake Perris is owned and managed by the California Department of Water Resources as a drinking-water supply reservoir. Inflows to the reservoir are from the eastern branch of the California Aqueduct, and water enters the reservoir from a submerged inlet structure located 23 m below the surface in the northwest corner adjacent to the dam. The inflows are controlled by the MWDSC. Lake Perris has a maximum pool volume of approximately 162 million m³ and a maximum surface area of approximately 9.4 million m². Recreation on the lake is managed by the California Department of Parks and Recreation. Recreational boating activity is year-round and limited to 450 boats on the lake at any one time, with approximately 75 percent of the boats currently using two-stroke marine engines (McCord and Schladow, 1998). The MWDSC has collected approximately 3 to 4 years of VOC data, including data for MTBE (June 1996 through September 1999).

Average wind speed, air temperature, atmospheric pressure, epilimnion depth, epilimnion temperature, and air VOC concentrations were used for calibration and verification. The averages for input parameters were calculated on the basis of the time scale (daily, weekly, or monthly) required for the simulations. The average meteorological input parameters were obtained in 1999 from EarthInfo, Inc (1996a, 1996b) for Perris, California. The epilimnion depths, water temperatures, lake depths, and lake DO and MTBE concentrations were obtained from MWDSC

(1999). Atmospheric concentrations of MTBE were obtained from the California Environmental Protection Agency, Air Resources Board (CA-ARB) (1998) for Long Beach, Anaheim, Upland, and Fontana, California (nearest air quality monitoring sites to Lake Perris). Lake inflows and outflows were obtained from the California Department of Water Resources (1999). Appendix B presents model input parameters for Lake Perris, California, and Appendix C presents model output files.

Lake-Stratification and Lake-Volume Simulations

Dissolved oxygen was used to calibrate Lake Perris hydrodynamics using the LakeVOC model for June 1996 through December 1998. Dissolved oxygen concentrations were simulated using the same model assumptions as used for VOC concentrations. Model calibration of estimated-to-measured DO concentrations was completed by adjusting the values of the epilimnion depth within the thermocline and applying a first-order degradation rate for DO in the hypolimnion when the lake was stratified (May through September). The first-order degradation rates for DO were developed from the measured concentrations in the hypolimnion. Once the model calibration was completed, a comparison was made of measured in relation to estimated depths and volumes for both the epilimnion and hypolimnion.

Simulation 10: The simulation reproduced the general features of seasonal variation of DO within the reservoir. The difference between the measured epilimnion depths and the calibrated epilimnion depths ranged from 0 to 3.15 m. The differences in the epilimnion depths were within the range of the measured thermocline of the stratified reservoir. The measured DO concentrations were averaged on a depth-weighted basis lakewide within the epilimnion and hypolimnion to obtain a single value for each layer within the reservoir. The difference between the measured depth-averaged and model-estimated concentrations for DO ranged from -1.4 mg/L (-19 percent), April 1997, to 3.2 mg/L (34 percent), December 1996, and -1.6 mg/L (-48 percent), November 1998, to 5.8 mg/L (89 percent), October 1997, in the epilimnion and hypolimnion, respectively (fig. 4).

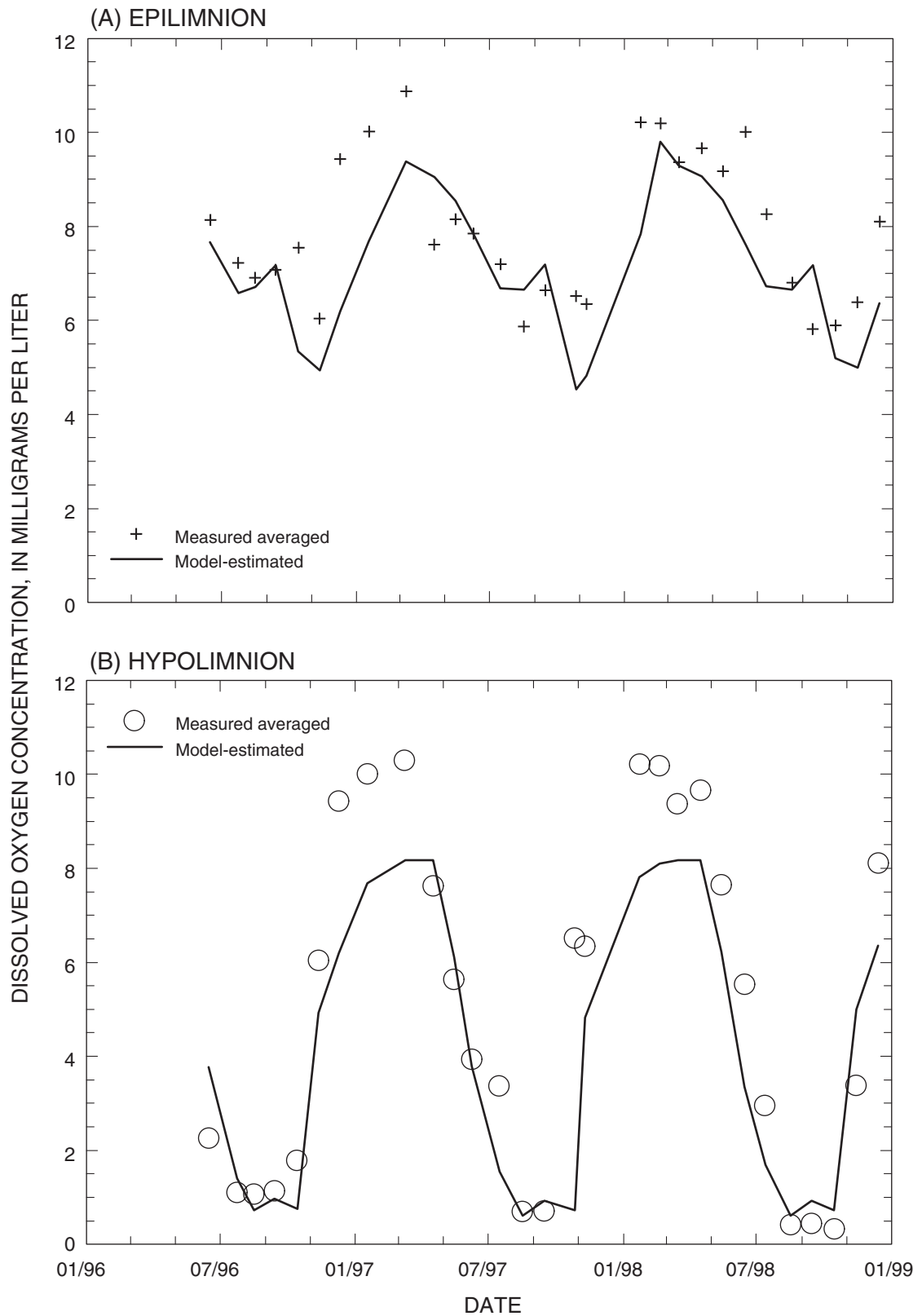


Figure 4. Measured-averaged and model-estimated dissolved oxygen concentrations in the (A) epilimnion and (B) hypolimnion, Lake Perris, California, June 1996 through December 1998.

As a check of the hydrodynamics calibration, the measured lake epilimnion and hypolimnion volumes were compared with the model-estimated volumes. The volumes compared well, with the model-estimated daily and monthly average volumes not changing as rapidly as the measured volumes but following the observed trend (figs. 5 and 6). The large drop in the epilimnion volume and large increase in the hypolimnion volume near the end of January 1997 in figure 5 are associated with lake destratification (turnover). The median differences between the measured volume and the model-estimated volume were -4.0 and 0.0 percent for the epilimnion and hypolimnion, respectively, from June 1996 through September 1997. Based on the median differences and the large range between measured and model-estimated volumes (fig. 6) in both the epilimnion and hypolimnion, the model reasonably estimates the volumes in the lake.

VOC Concentration Simulations

Boating activity and estimated mass-emission rates from marine engines were used to estimate the concentrations of MTBE in the epilimnion and hypolimnion of Lake Perris using the LakeVOC model. California Park Service (California Park Service, written commun., February 16, 1999) information was used to estimate the number of boats using the main boat ramps at Lake Perris. A marine-engine mass-emission rate of 5.5 μg of MTBE per boat per hour was assumed and based on the estimates made by Anderson (1997) specifically for Lake Perris. The emission-rate estimate by Anderson (1997) assumed 2 hours of boating operation per boat per day and an average for all two-cycle and four-cycle marine engines, with the majority of emissions from two-cycle marine engines. The California Park Service boat count estimates and the Anderson (1997) mass-emission rate were combined to estimate the temporal MTBE mass-load inputs for Lake Perris. The atmospheric MTBE concentration inputs were averaged from the four nearest CA-ARB sites.

The measured MTBE concentrations, from MWDS, in the reservoir were averaged for the monitoring date, vertically over the calibrated epilimnion and hypolimnion depths and spatially across the reservoir to obtain an average concentration for each of the two layers within the reservoir. These measured-averaged concentrations were used for the comparisons to the model-estimated MTBE concentrations using daily, weekly, and monthly time series for required model inputs.

Simulation 11: This simulation verified that the LakeVOC model reasonably estimated the concentration of MTBE in Lake Perris, especially in the epilimnion. The model was calibrated with 1.5 years of data (June 1996 to December 1997) and verified with a different, but similar, period of data (January 1998 to September 1999). Calibration was done by adjusting the emission estimate by Anderson (1997) and applying it to the daily, weekly, or monthly boat use for the calibration time-period to get daily VOC inputs to the lake.

Daily Simulation

The calibration and verification measured-averaged and model-estimated concentrations from daily model inputs are compared in figures 7 and 8. The model calibration for daily model inputs produced differences for the measured-averaged and model-estimated MTBE concentrations ranging from -3.2 $\mu\text{g}/\text{L}$ (-16.6 percent, based on the measured-averaged concentration) to 9.5 $\mu\text{g}/\text{L}$ (61 percent) with a median difference of 0.15 $\mu\text{g}/\text{L}$ for the epilimnion (fig. 7A) and -3.6 $\mu\text{g}/\text{L}$ (-341 percent) to 5.9 $\mu\text{g}/\text{L}$ (65 percent) with a median difference of -1.1 $\mu\text{g}/\text{L}$ for the hypolimnion (fig. 7B). Based on the median difference and the large range in the model-estimated concentrations in the epilimnion (fig. 8A), the model calibrated reasonably well for the epilimnion. In contrast, a narrow range in the model-estimated concentrations is evident for the hypolimnion (fig. 8B). The poorer calibration in the hypolimnion could be caused by the model not characterizing episodic mixing events across the thermocline or mixing that does not change the mean mixed layer depths.

The verification step produced concentration differences between the measured-averaged and model-estimated MTBE concentrations, from the calibrated daily model inputs, that ranged from -10.6 $\mu\text{g}/\text{L}$ (-217 percent) to 9.2 $\mu\text{g}/\text{L}$ (34 percent) with a median difference of -2.5 $\mu\text{g}/\text{L}$ for the epilimnion (fig. 7A) and -4.0 $\mu\text{g}/\text{L}$ (-630 percent) to 2.2 $\mu\text{g}/\text{L}$ (37 percent) with a median difference of -1.1 $\mu\text{g}/\text{L}$ for the hypolimnion (fig. 7B). As shown in figure 7, a seasonal variation of the concentration differences occurs with larger concentration differences in both the epilimnion and hypolimnion occurring during the summer or high-use time period when MTBE concentrations are highest. Part of the larger differences in the verification process were likely caused by the lack of complete boat use information (compared to the calibration time period) and, possibly, to a partial fleet changeover to newer marine engine technology during the verification time period.

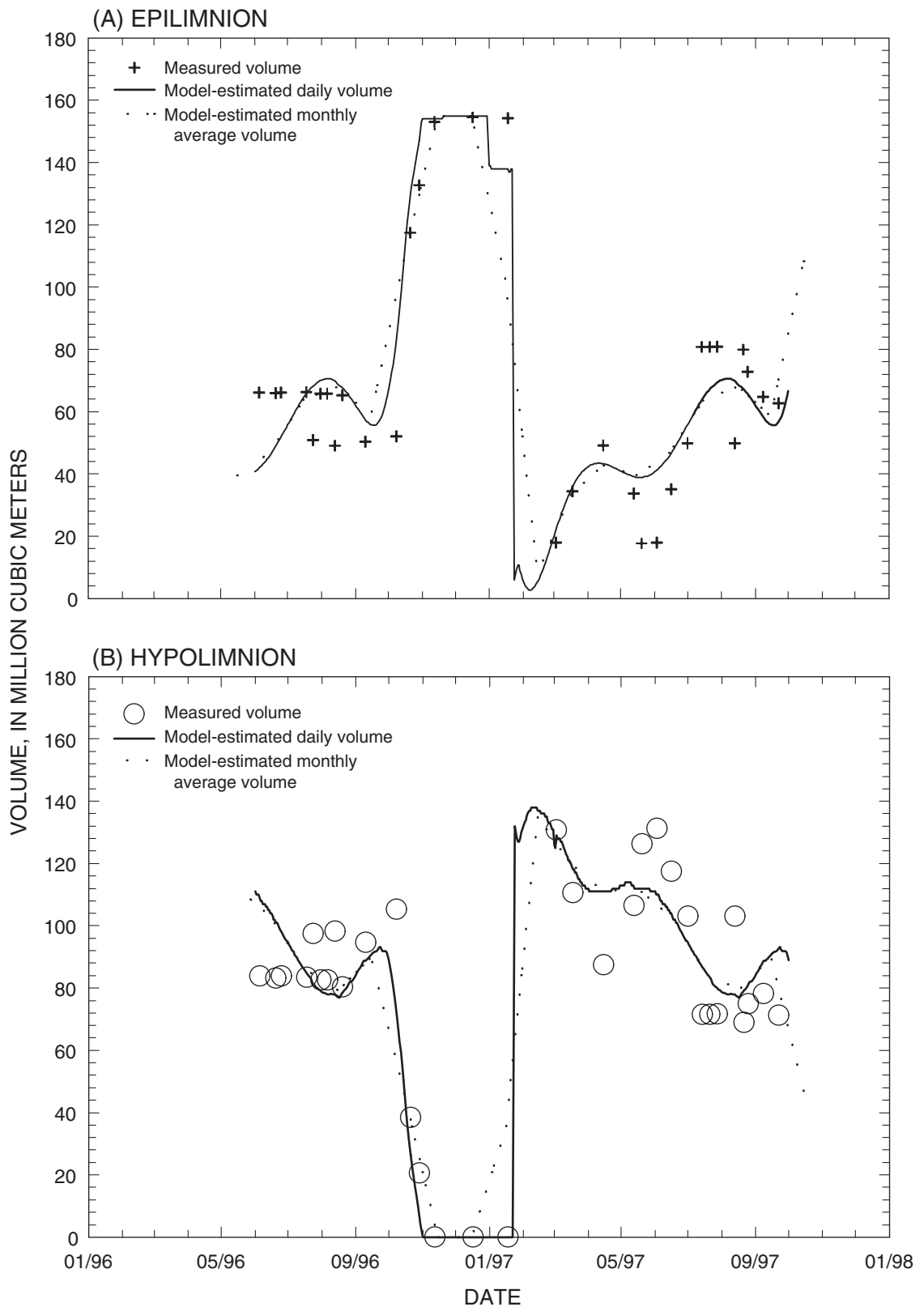


Figure 5. Comparison of measured and model-estimated daily and monthly-averaged lake volumes in the (A) epilimnion and (B) hypolimnion, Lake Perris, California, June 1996 through September 1997.

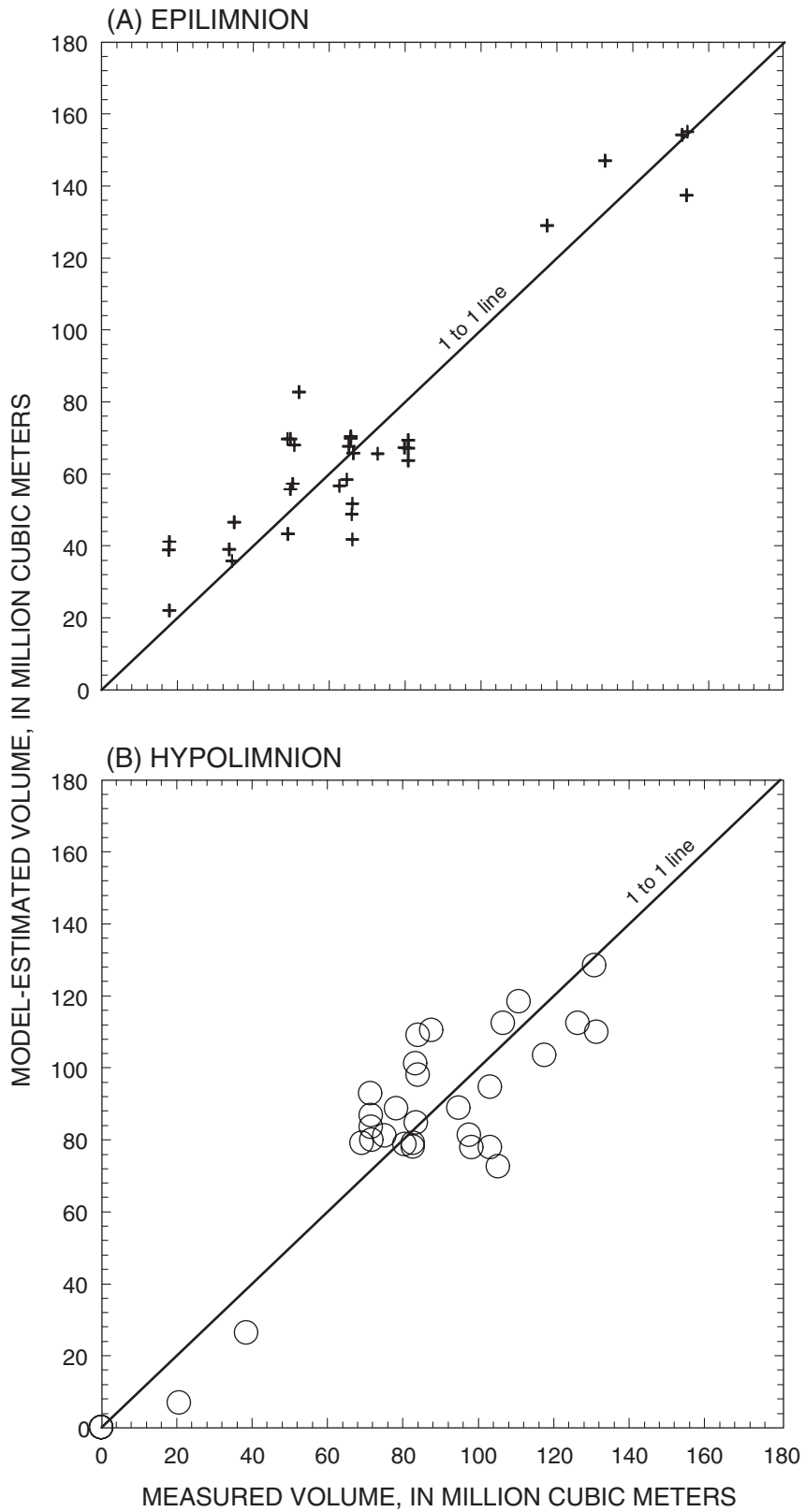


Figure 6. Comparison of measured and model-estimated daily lake volumes in the (A) epilimnion and (B) hypolimnion, Lake Perris, California, June 1996 through September 1997.

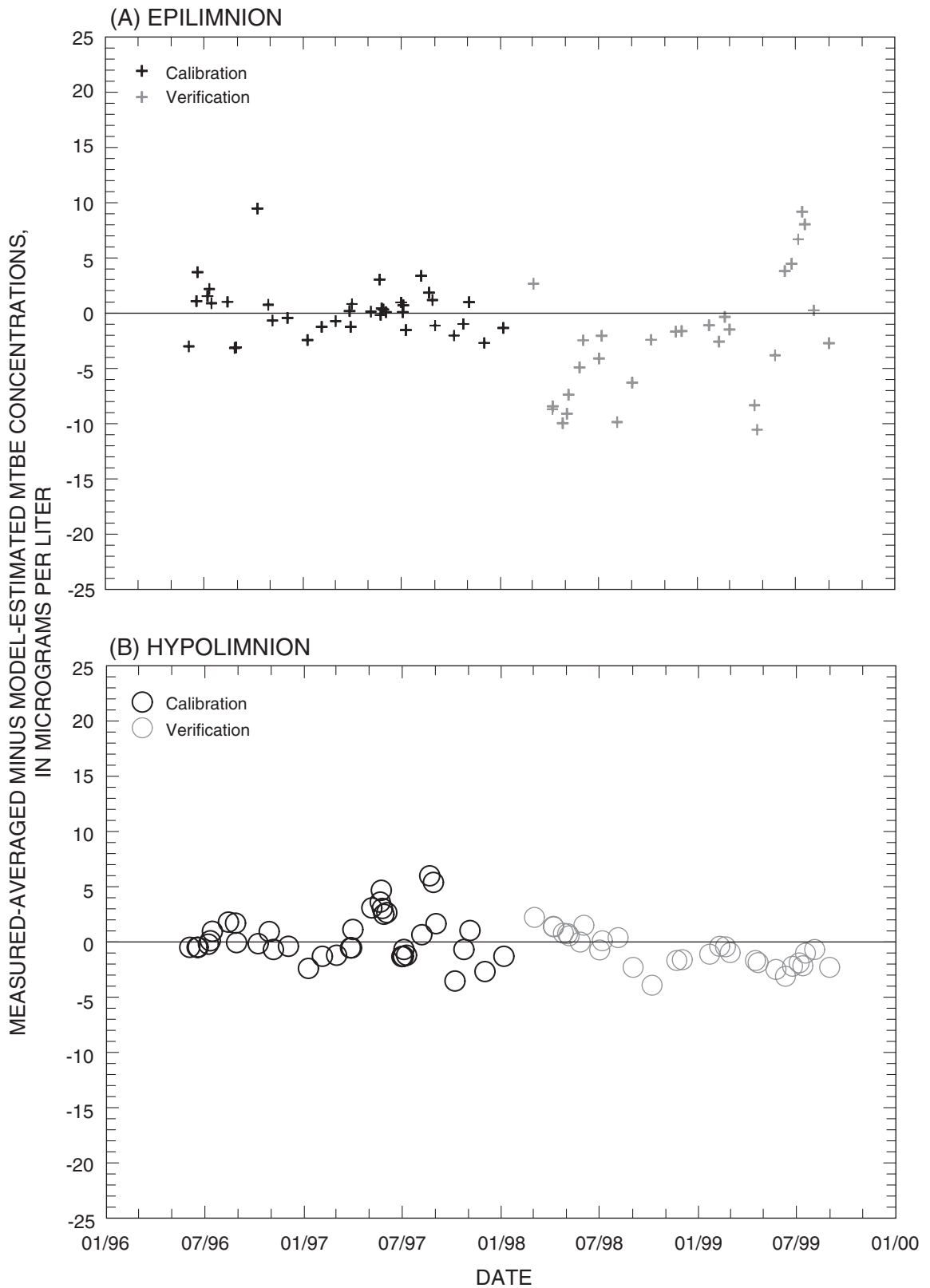


Figure 7. Differences in measured-averaged minus model-estimated MTBE concentrations from daily model inputs in the (A) epilimnion and (B) hypolimnion, Lake Perris, California, June 1996 through September 1999.

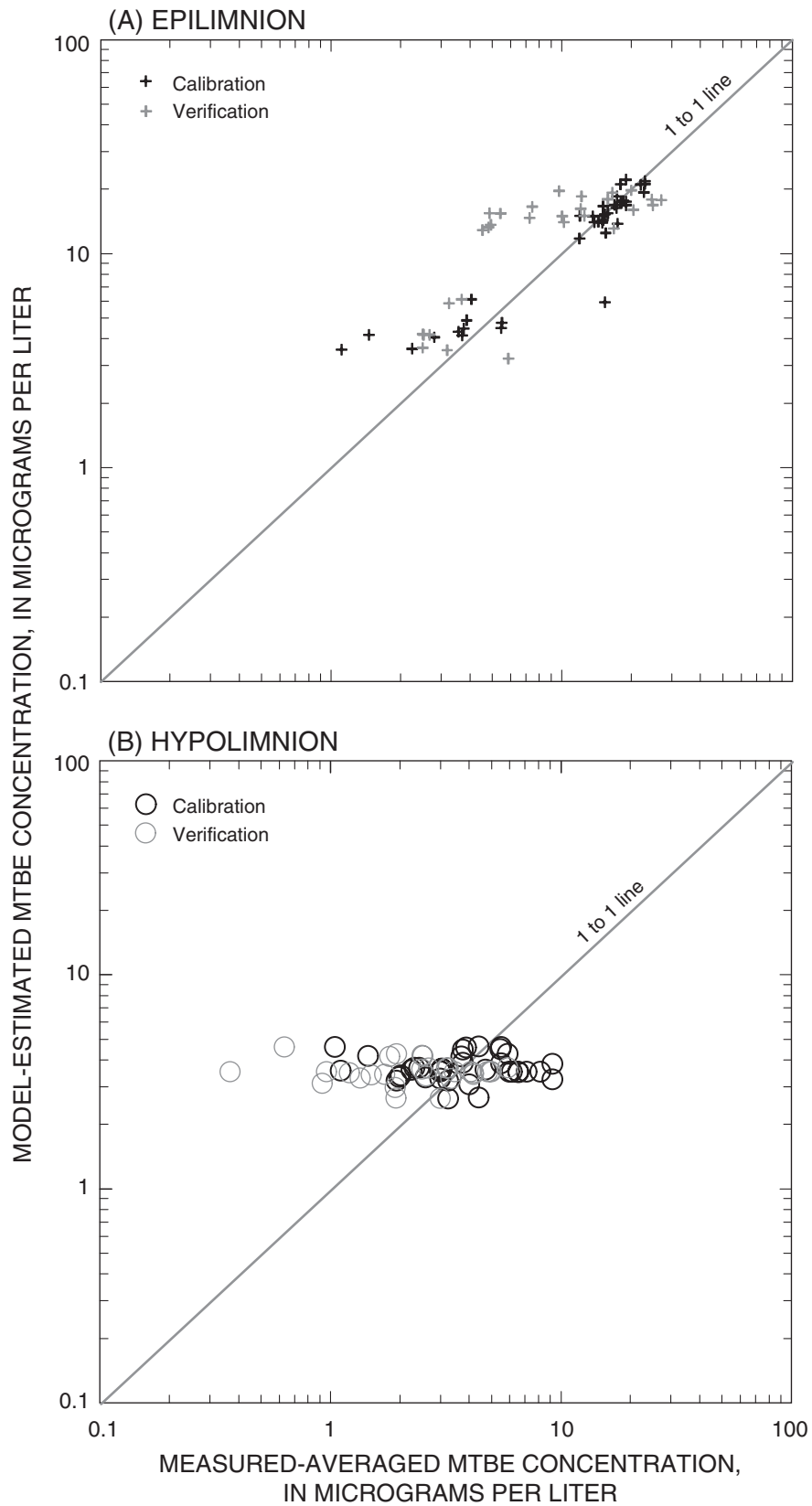


Figure 8. Comparison of model-estimated and measured-averaged MTBE concentrations from daily model inputs in the (A) epilimnion and (B) hypolimnion, Lake Perris, California, June 1996 through September 1999.

Weekly Simulation

Weekly VOC model inputs were calculated by applying the calibrated emission estimates to the weekly boat use. The calibration and verification measured-averaged and model-estimated MTBE concentrations for weekly model inputs are compared in figures 9 and 10. The model calibration for weekly model inputs produced MTBE concentration differences between the measured-averaged and model-estimated concentrations ranging from -3.3 µg/L (-19 percent, based on the measured-averaged concentration) to 9.0 µg/L (59 percent) with a median difference of 0.29 µg/L for the epilimnion (fig. 9A) and -5.4 µg/L (-515 percent) to 4.6 µg/L (50 percent) with a median difference of -1.0 µg/L for the hypolimnion (fig. 9B). Based on the median differences and the large range in the model-estimated concentration in the epilimnion (fig. 10A), the model calibrated reasonably well for the epilimnion. In contrast, a narrow range in the model-estimated concentrations is evident in the hypolimnion (fig. 10B) especially at low MTBE concentrations. The poorer calibration in the hypolimnion could be caused by the model not characterizing episodic mixing events across the thermocline or mixing that does not change the mean mixed layer depths.

The verification step produced concentration differences for the measured-averaged and model-estimated MTBE concentrations, from the calibrated weekly model inputs, that ranged from -10 µg/L (-206 percent) to 9.1 µg/L (34 percent) with a median difference of -2.5 µg/L for the epilimnion (fig. 9A) and -5.8 µg/L (-919 percent) to 1.9 µg/L (32 percent) with a median difference of -1.7 µg/L for the hypolimnion (fig. 9B). The calibration and verification using weekly model inputs overestimated the concentrations in the epilimnion, as compared to the daily simulation. A similar seasonal variation in the concentration differences as seen in figure 7 was observed as the time scale was increased from daily to weekly. As the time scale of the model inputs is increased, the median and range of differences between the measured-averaged and model-estimated concentrations generally increased, especially for the hypolimnion.

Monthly Simulation

Monthly VOC inputs were calculated by applying the calibrated daily emission estimates to the monthly boat use. The calibration and verification measured-averaged and model-estimated MTBE concentrations for monthly model inputs are compared in figures 11 and 12. The model calibration for monthly model inputs produced MTBE concentration differences for the measured-averaged and model-estimated concentrations ranging from -15 µg/L (-84 percent, based on the measured-averaged concentration) to 2.2 µg/L (14 percent) with a median difference of -9.3 µg/L for the epilimnion (fig. 11A) and -7.6 µg/L (-731 percent) to 2.7 µg/L (30 percent) with a median difference of -2.7 µg/L for the hypolimnion (fig. 11B). Based on the median difference and the large range in the model-estimated concentrations in the epilimnion (fig. 12A), the model calibrated reasonably well for the epilimnion. In contrast, a narrow range in the model-estimated concentrations is evident for the hypolimnion (fig. 12B). As noted previously, the poorer calibration in the hypolimnion could be caused by the model not characterizing episodic mixing events across the thermocline or mixing that does not change the mean mixed layer depths.

The verification step produced concentration differences for the measured-averaged and model-estimated MTBE concentrations, from the calibrated monthly model inputs, that ranged from -22 µg/L (-228 percent) to -0.7 µg/L (-2.6 percent) with a median difference of -11 µg/L for the epilimnion (fig. 11A) and -8.1 µg/L (-1,280 percent) to 0.5 µg/L (7.9 percent) with a median difference of -3.7 µg/L for the hypolimnion (fig. 11B). The calibration and verification using monthly model inputs further overestimated the concentrations in the epilimnion, as compared to the daily and weekly simulations. A similar seasonal variation in the concentration differences as seen in figures 7 and 9 was observed as the time scale was increased to monthly input variables. As the time scale of the model inputs is increased the median and range of differences between the measured-averaged and model-estimated concentrations increased, especially for the hypolimnion.

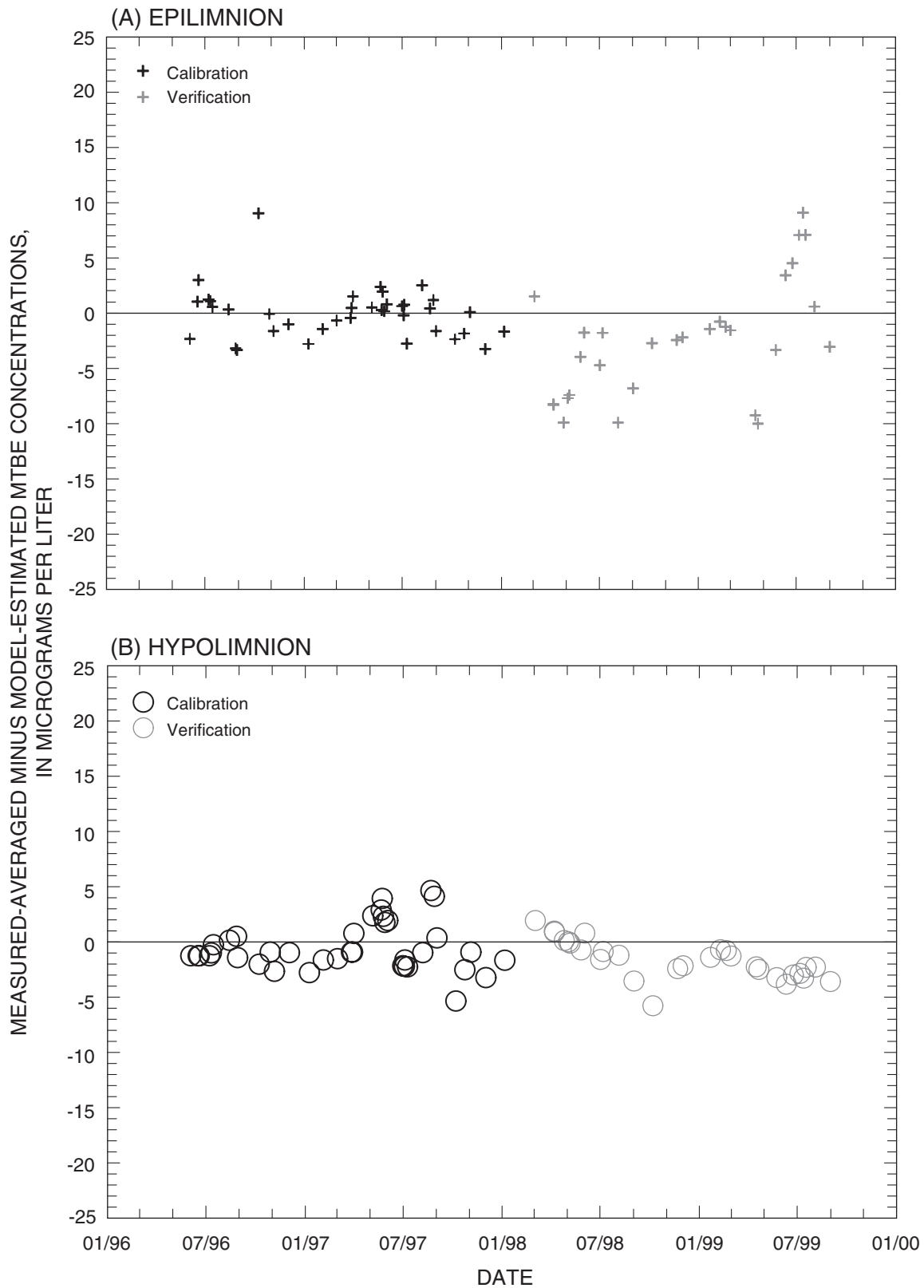


Figure 9. Differences in measured-averaged minus model-estimated MTBE concentrations from weekly model inputs in the (A) epilimnion and (B) hypolimnion, Lake Perris, California, June 1996 through September 1999.

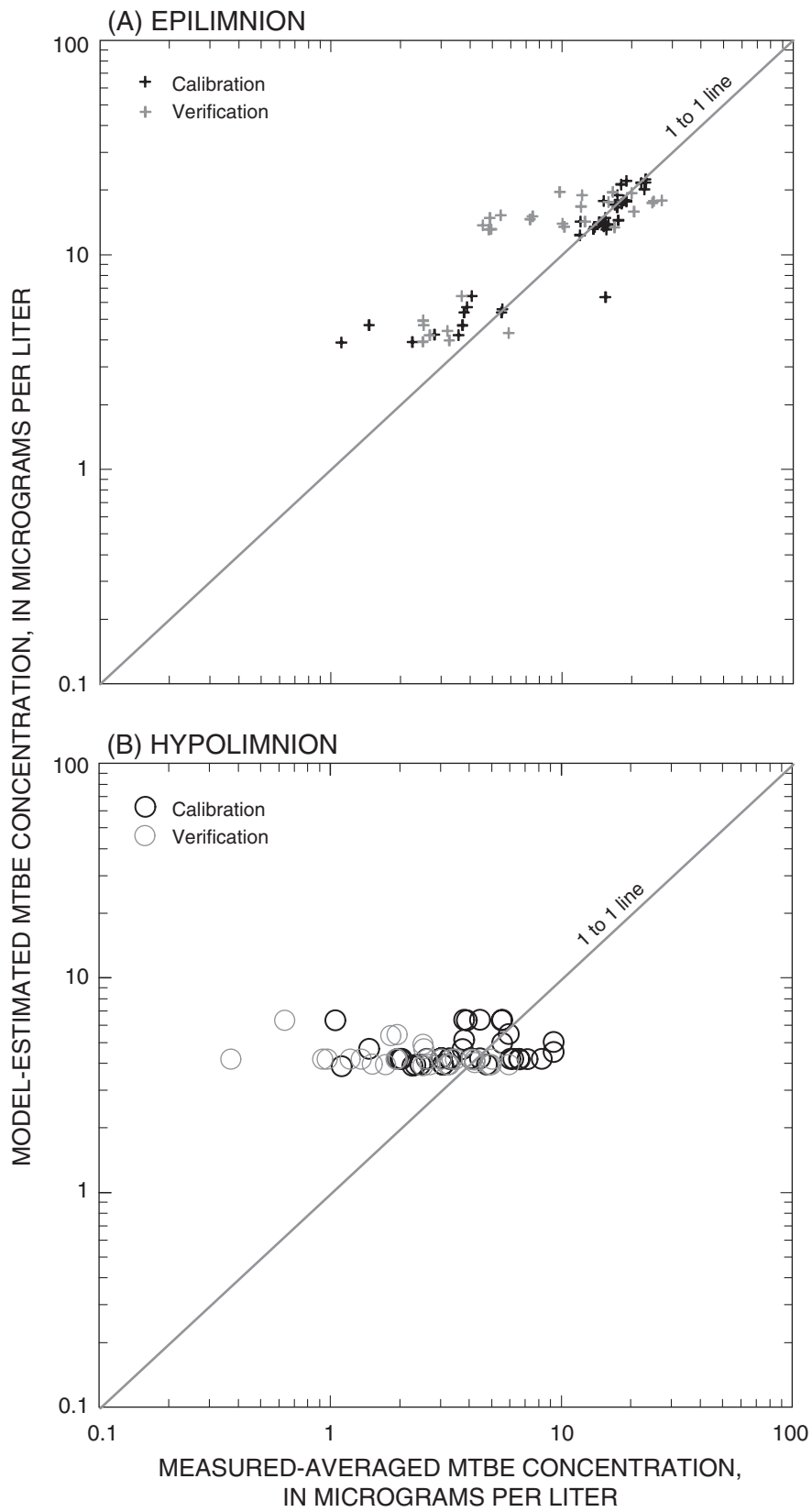


Figure 10. Comparison of model-estimated and measured-averaged MTBE concentrations from weekly model inputs in the (A) epilimnion and (B) hypolimnion, Lake Perris, California, June 1996 through September 1999.

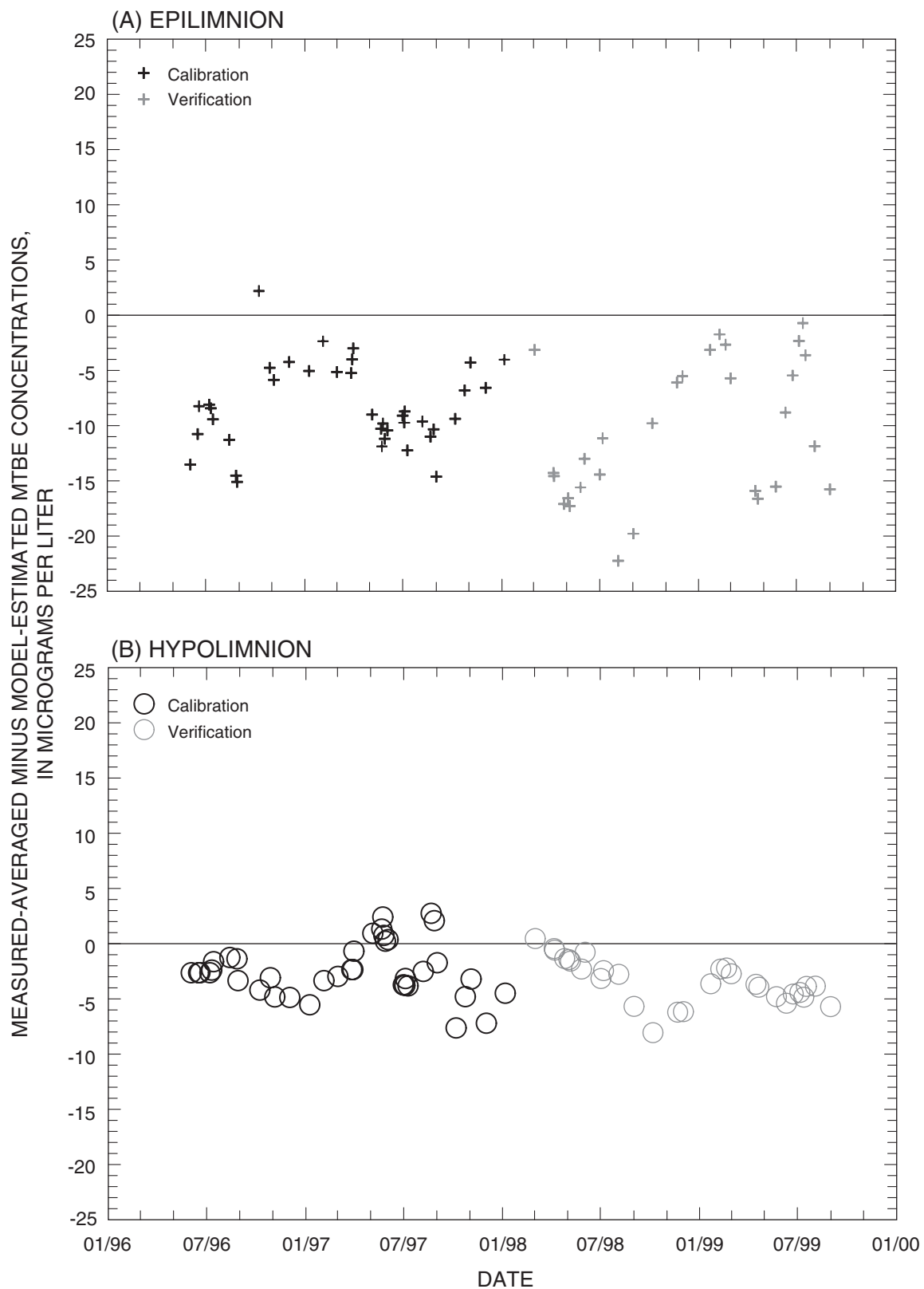


Figure 11. Differences in measured-averaged minus model-estimated MTBE concentrations from monthly model inputs in the (A) epilimnion and (B) hypolimnion, Lake Perris, California, June 1996 through September 1999.

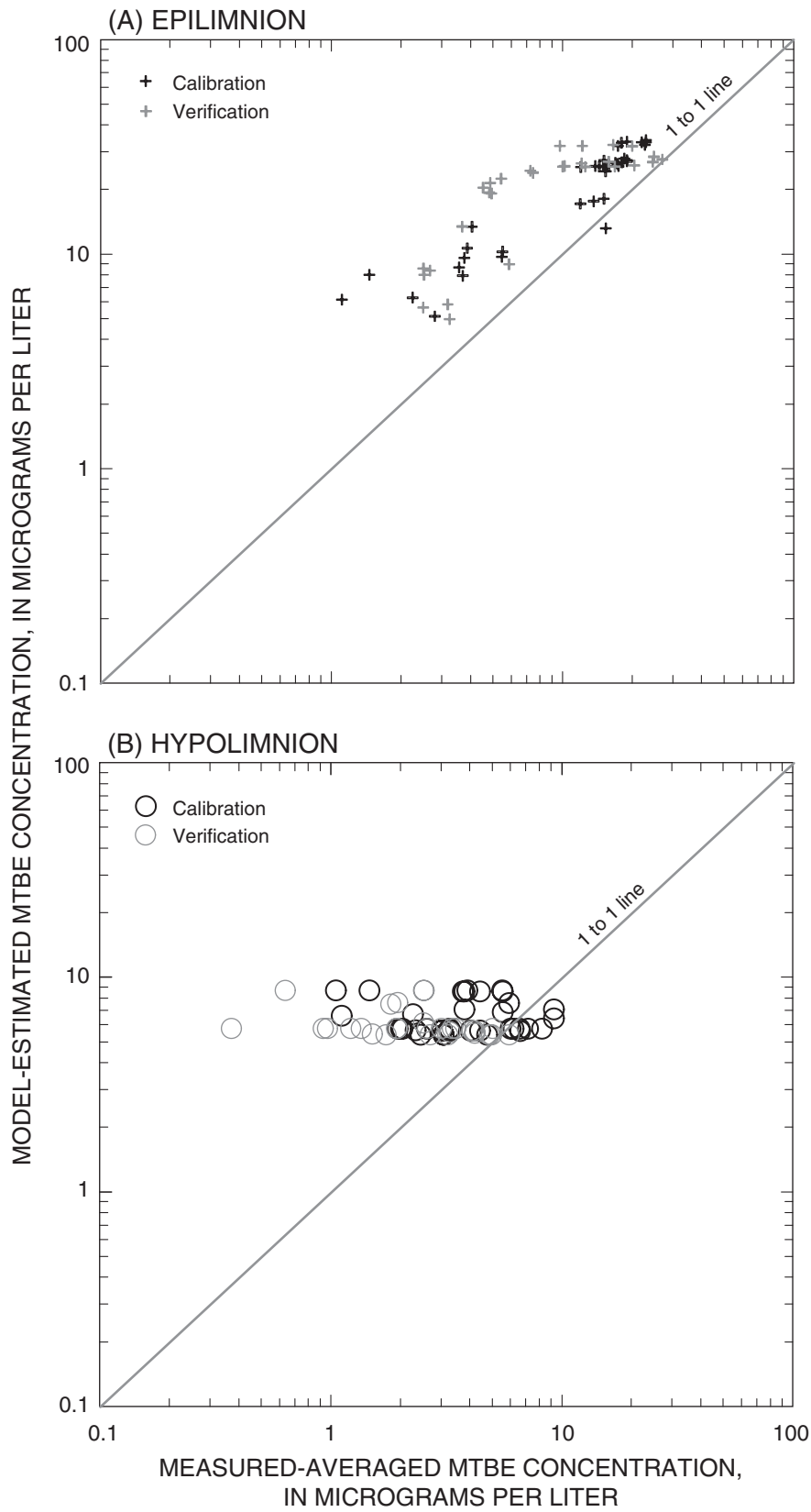


Figure 12. Comparison of model-estimated and measured-averaged MTBE concentrations from monthly model inputs in the (A) epilimnion and (B) hypolimnion, Lake Perris, California, June 1996 through September 1999.

SUMMARY

This report documents LakeVOC, a model to estimate the concentration of a VOC in lakes and reservoirs. A two-layer system is modeled on the basis of mixing between the two layers with volatilization to and absorption from the atmosphere. The LakeVOC model input parameters include wind speed, air temperature, atmospheric pressure, relative humidity, lake depth in relation to lake-surface area profile, epilimnion temperature, epilimnion depth, inflow rate and inflow depth, outflow rate and outflow depth, VOC inputs to the lake, atmospheric VOC concentrations, and degradation rates, diffusivity, solubility, molecular weight, and an initial concentration of the VOC of interest.

The LakeVOC model estimates the concentrations of VOCs in lakes and reservoirs adequately given a minimum of available information. The model hydrographical and meteorological inputs are available from monitoring programs and weather stations. The VOC inputs from the atmosphere may be available from air-quality monitoring programs located near the lake or reservoir. The boating inputs can be calculated on the basis of available information from the recreational management agency for the lake or reservoir.

The model was verified using a series of nine controlled simulations designed to test the characterizations of conservation of mass, air-water gas exchange, mixing between the epilimnion and hypolimnion, evaporation, and volume changes due to inflow and outflow. The model was verified further for an actual water-supply reservoir, Lake Perris, Riverside County, California by two additional simulations. The two additional simulations assessed the LakeVOC model's ability to estimate: (1) the depth and volumes of the epilimnion and hypolimnion, and (2) MTBE concentrations based on daily, weekly, and monthly model input parameters.

Collectively, the simulations based on daily model input parameters showed that the LakeVOC model adequately estimated concentrations for the epilimnion with a larger variation between the measured-averaged and model-estimated values for the hypolimnion. The poorer calibration in the hypolimnion could be caused by the model not characterizing episodic mixing events across the thermocline or mixing that does not change the mean mixed layer depths. As the time scale of the model inputs increased (daily to weekly to monthly), the median and range of differences between the measured-averaged concentrations

and the model-estimated concentrations increased, especially for the hypolimnion. This may be because as the time scale is increased from daily to weekly to monthly, the averaging of model inputs causes increased loss of detail in the model estimates. Because of the increasing differences as the time scale is increased, verification results indicate that the model produces the most accurate estimates when daily inputs are used. In general, the larger differences between the measured-averaged and model-estimated concentrations in the verification simulations were likely caused by the lack of complete boat use information and, possibly, to a partial fleet changeover to newer marine engine technology during the validation time-period.

REFERENCES

- Anderson, Michael, 1997, Predicted MTBE concentrations in the Eastside Reservoir: Soil and Environmental Science, April, p. 2-7.
- Atkins, P.W., 1986, Physical chemistry: New York, W.H. Freeman and Co., 857 p.
- Baehr, A.L., and Reilly, T.J., 2001, Water quality at lakeside communities in Sussex and Morris Counties, New Jersey, 1998-1999, with emphasis on methyl *tert*-butyl ether (MTBE) and other fuel related compounds: U.S. Geological Survey Water-Resources Investigation Report 01-4149, 86 p.
- Baehr, A.L., and Zapecza, O.S., 1998, Methyl *tert*-butyl ether (MTBE) and other volatile organic compounds in lakes in Byram Township, Sussex County, New Jersey, summer 1998: U.S. Geological Survey Water-Resources Investigation Report 98-4264, 8 p.
- Boughton, C.J., and Lico, M.S., 1998, Volatile organic compounds in Lake Tahoe, Nevada and California, July-September 1997: U.S. Geological Survey Fact Sheet 055-98, 2 p.
- California Department of Water Resources, Division of Operations and Maintenance, 1999, State water project monthly operations data for 1996, 1997: electronic data files accessed on March 18, 1999, at URL <http://www.wco.water.ca.gov/monthly/monthly.menu.html>
- California Environmental Protection Agency, Air Resources Board, 1998, Toxics data request; 1990-1997: Sacramento, California [digital data file].
- Dale, M.S., Koch, Bart, Losee, R.F., Crofts, E.W., and Davis, M.K., 2000, MTBE in southern California water—Motorized recreational watercraft were the predominant mode of contamination in reservoirs: Journal of the American Water Works Association, v. 92, no. 8, p. 42-51.

- Dewulf, J., Drijvers, D., and Van Langenhove, H., 1995, Measurement of Henry's law constant as function of temperature and salinity for the low temperature range: *Atmospheric Environment*, v. 29, no. 3, p. 232-331.
- EarthInfo, Inc., 1996a, NCDC summary of the day: Boulder, Colorado, EarthInfo, Inc. [CDROM].
- 1996b, NCDC surface airways: Boulder, Colorado, EarthInfo, Inc. [CDROM].
- Gabele, P.A., and Pyle, S.M., 2000, Emissions from two outboard engines operating on reformulated gasoline containing MTBE: *Environmental Science and Technology*, v. 34, no. 4, p. 368-372.
- Hayduk, W., and Laudie, H., 1974, Prediction of diffusion coefficients for nonelectrolytes in dilute aqueous solutions: *American Institute of Chemical Engineering*, v. 20, no. 3, p. 611-615.
- Howard, P.H., Boethling, R.S., Meylan, W.M., and Michalenko, E.M., 1991, *Handbook of environmental degradation rates*: Chelsea, Michigan, Lewis Publishers, Inc., 725 p.
- Jackivicz, T.J., Jr., and Kuzminski, L.N., 1973, A review of outboard motor effects on the aquatic environment: *Journal of the Water Pollution Control Federation*, v. 45, no. 8, p. 1759-1770.
- Jüttner, Friedrich, 1988, Motor-boat-derived volatile organic compounds (VOC) in lakewater: *Z. Wasser-Abwasser-Forsch.*, v. 21, p. 36-39.
- 1994, Emission of aromatic hydrocarbons and aldehydes into the water by a four-stroke outboard motor—Quantitative measurements: *Chemosphere*, v. 29, no. 2, p. 191-200.
- Jüttner, Friedrich, Backhaus, Diedrich, Matthias, Uwe, Essers, Ulf, Greiner, Rolf, and Mahr, Bernd, 1995a, Emissions of two- and four-stroke outboard engines—I. Quantification of gases and VOC: *Water Research*, v. 29, no. 8, p. 1976-1982.
- 1995b, Emissions of two- and four-stroke outboard engines—II. Impact on water quality: *Water Research*, v. 29, no. 8, p. 1983-1987.
- Leighton, D.T., and Calo, J.M., 1981, Distribution coefficients of chlorinated hydrocarbons in dilute air-water systems for groundwater contamination applications: *Journal of Chemical Engineering Data*, v. 26, no. 4, p. 382-385.
- Lewis, W.K., and Whitman, W.G., 1924, *Principles of gas adsorption*: Industrial and Engineering Chemistry, v. 16, no. 12, p. 1215-1220.
- Lico, M.S., and Pennington, Nyle, 1999, Concentrations and distribution of manmade organic compounds in the Lake Tahoe Basin, Nevada and California, 1997-99: U.S. Geological Survey Water-Resources Investigations Report 99-4218, 12 p.
- Mackay, D., Shiu, W.Y., and Ma, K.C., 1992, *Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals—V. I. Monoaromatic hydrocarbons, chlorobenzenes, and PCBs*: Chelsea, Michigan, Lewis Pub., Inc., 697 p.
- 1993, *Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals—V. III. Volatile organic chemicals*: Chelsea, Michigan, Lewis Pub., Inc., 916 p.
- Mahler, B.J., 2000, Determining the occurrence of pesticides and volatile organic compounds in public water-supply source waters in Texas: U.S. Geological Survey Fact Sheet 010-00, 2 p.
- McCord, S.A., and Schladow, S.G., 1998, Transport and fate modeling of MTBE in lakes and reservoirs, *in* Arturo Keller, Ph.D., John Froines, Ph.D., Catherine Koshland, Ph.D., John Reuter, Ph.D., Irwin (Mel) Suffet, Ph.D., Jerold Last, Ph.D., eds., *Health and environmental assessment of MTBE*, chapter IV—Ground and surface water: Sacramento, California, State of California, 38 p.
- Metropolitan Water District of Southern California, 1999, Data Request: LaVerne, California [digital data file].
- Press, W.H., Flannery, B.P., Teukolsky, S.A., and Vetterling, W.T., 1992, *Numerical recipes in FORTRAN: The art of scientific computing* (2nd ed.): New York, Cambridge University Press, 963 p.
- Rathbun, R.E., 1998, Transport, behavior, and fate of volatile organic compounds in streams: U.S. Geological Survey Professional Paper 1589, 151 p.
- Reid, R.C., Prausnitz, J.M., and Poling, B.E., 1987, *The properties of gases and liquids* (4th ed.): New York, McGraw-Hill, 741 p.
- Reuter, J.E., Allen, B.C., Richards, R.C., Pankow, J.F., Goldman, C.R., Scholl, R.L., and Seyfried, J.S., 1998, Concentrations, sources, and fate of the gasoline oxygenate methyl *tert*-butyl ether (MTBE) in a multiple-use lake: *Environmental Science and Technology*, v. 32, no. 23, p. 3666-3672.
- Robbins, G.A., Wang, Suya, and Stuart, J.D., 1993, Using the static headspace method to determine Henry's law constants: *Analytical Chemistry*, v. 65, no. 21, p. 3113-3118.
- Schwarzenbach, R.P., Gschwend, P.M., and Imboden, D.M., 1993, *Environmental organic chemistry*: New York, Wiley-Interscience, 681 p.
- van Donkelaar, P., 1988, Comments on an article by Friedrich Jüttner "Motor-boat-derived volatile organic compounds (VOC) in lakewater": *Z. Wasser-Abwasser-Forsch.*, v. 21, p. 255-256.
- Wanninkhof, R., 1992, Relationship between wind speed and gas exchange over the ocean: *Journal of Geophysical Research*, v. 97, no. C5, p. 7373-7382.

Wanninkhof, R., Ledwell, J., and Crusius, J., 1991, Gas transfer velocities on lakes measured with sulfur hexafluoride, *in* Wilhelms, S.C., and Gulliver, J.S., eds., Air-water mass transfer: New York, American Society of Civil Engineering, p. 441-458.

Weast, R.C., 1983, CRC handbook of chemistry and physics: Boca Raton, Florida, CRC Press Inc., 2,381 p.
Wilke, C.R., and Chang, P., 1955, Correlation of diffusion coefficients in dilute solutions: American Institute of Chemical Engineering Journal, v. 1, p. 264-270.