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Production and consumption of methyl halides in a freshwater lake

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Abstract

The concentrations of the methyl halides CH_3Cl and CH_3Br in Lake Washington and its tributary streams were measured during the period 1994–1998. Strong seasonal variation was observed. In summer, the surface mixed layer in the middle of the lake was found to be generally undersaturated for CH_3Cl but consistently supersaturated for CH_3Br relative to air–water gas equilibrium; meanwhile, the deep waters ($z_{max} = 65$ m) of the summertime lake were found to be depleted to near zero levels for both compounds. In winter, the methyl halides were observed to be vertically well mixed throughout the water column and strongly undersaturated in both species. A simple mass-balance box model indicates that the wintertime lake ($T = 8°C$) is a net sink for atmospheric methyl halides with estimated loss rates of $\sim$2.6–3.2 pM d^{-1} for CH_3Cl (1 pM = 10^{-12} mol L^{-1}) and 0.09–0.13 pM d^{-1} for CH_3Br, probably because of unspecified microbiological processes. In summer, the mass balance model indicates that there is a net source of CH_3Br in the surface mixed layer (0.17–0.25 pM d^{-1}), as required to maintain the observed strong supersaturation. However, the summer surface waters are apparently a sink for CH_3Cl, (1.9–2.9 pM d^{-1}), with enhanced biological production compensated by larger combined microbial and chemical sinks terms. In summer, methyl halide concentrations in the deep waters continue to decrease exponentially at the observed wintertime rate, while both production and loss rates in the surface waters are likely much faster than in winter, resulting in much shorter turnover timescales. An order-of-magnitude extrapolation of these Lake Washington methyl halide fluxes to a global source/sink from freshwater lakes implies a negligible contribution ($<$0.05%) with respect to the currently estimated global budgets of these gases.

CH_3Cl is the second largest source of Cl, and CH_3Br is the most abundant Br carrier to the stratosphere (Salawitch et al. 1988; Schauffler et al. 1993). Since halogenated compounds were first proposed to cause stratospheric ozone destruction (Molina and Rowland 1974; Wofsy et al. 1975), a number of studies have focused on the importance of naturally occurring methyl halides in this process. Following the detection of decreases in Antarctic ozone since 1980 (Farman et al. 1985), stratospheric ClO and BrO were determined to be major contributors to these losses (Anderson et al. 1989; DeZafra et al. 1989). Concern about possible anthropogenic inputs of atmospheric CH_3Br increased with the realization that Br is $\sim$60 times more effective per atom than Cl in removing ozone from the atmosphere (WMO 1998).

Major uncertainties remain in the global budgets for CH_3Cl and CH_3Br (Butler and Rodriguez 1996; Butler 2000). Based on recent studies, atmospheric CH_3Cl is believed to come largely from natural sources (Khalil and Rasmussen 1998; Khalil et al. 1998). The major identified sources are the surface ocean and biomass burning, and the major sink is the reaction with tropospheric OH. Additional sources of CH_3Cl may include tropical coastal land (Yokouchi et al. 2000), oxidation of organic material (Keppler et al. 2000), and release from salt marshes (Rhew et al. 2000).

For CH_3Br, approximately ⅔ of the flux to the atmosphere is thought to be from natural sources, the remainder due to anthropogenic sources (Butler and Rodriguez 1996). Early work indicated that the open ocean might be a major source of CH_3Br (Singh et al. 1983); however, more recent, extensive marine measurements indicate that the open ocean is a net sink for CH_3Br (Lobert et al. 1996). The role of the coastal ocean is still poorly defined. Other identified sources of CH_3Br are releases from salt marshes (Rhew et al. 2000), biomass burning, and industrial production of products for use as fumigants in agriculture and construction. Identified sinks of CH_3Br include the reaction with tropospheric OH, soil, and oceanic uptakes. The global evaluation based on the bromine latitudinal air sea transect (BLAST) measurements (Lobert et al. 1996) yields a net air-to-sea flux of CH_3Br of $\sim 21 \pm 10$ Gg yr^{-1} (1 Gg = 10^9 g). A more recent study by Groszko and Moore (1998) estimates a somewhat smaller sink of $\sim$3–13 Gg yr^{-1}. Shifting the ocean from a net source to a net sink worsens an already unbalanced budget and implies a missing terrestrial source, probably in the tropics (Butler and Rodriguez 1996; Khalil and Rasmussen 1998).

The chemical and biological processes that determine the saturation state of methyl halides at the sea surface remain poorly characterized. Recent research has shown that methyl halides are produced by a wide variety of marine phytoplankton (Scarratt and Moore 1996, 1998) and macroalgae (Manley and Dastoor 1988) and probably are consumed by (as yet uncharacterized) marine bacteria (King and Saltzman

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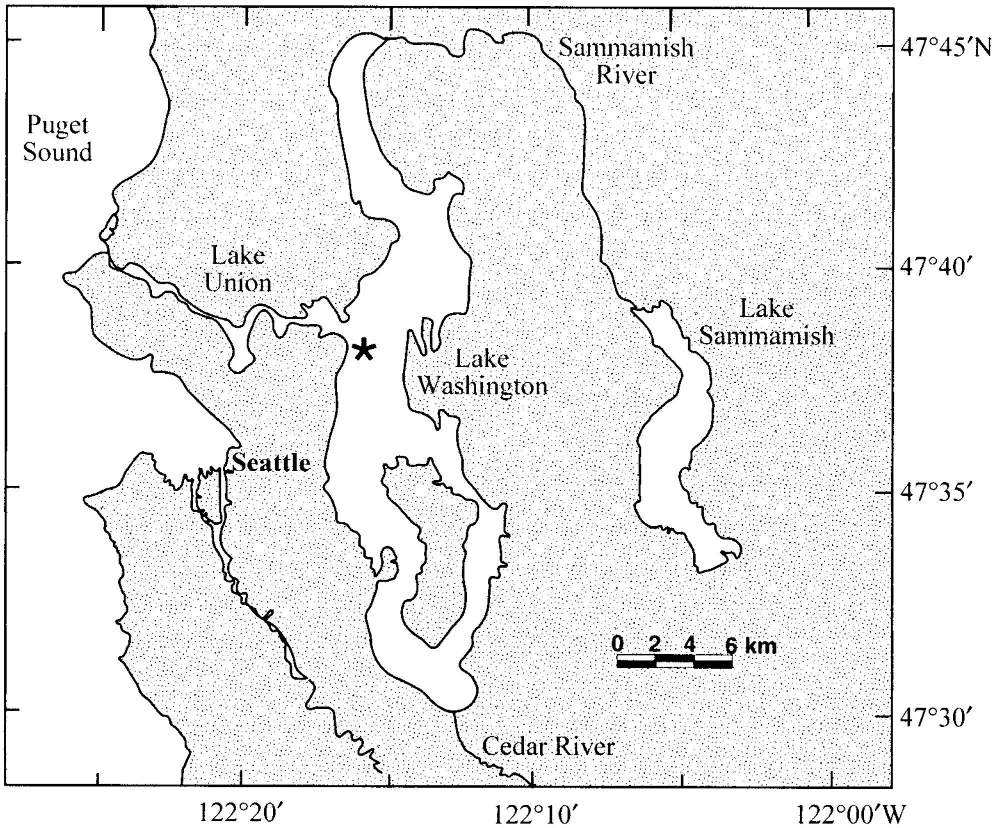

Fig. 1. Map of Lake Washington. Station location for vertical profiles is indicated (*).

1997). However, the calculated production rates, extrapolated from laboratory phytoplankton cultures, appear to be too slow to explain the observed oceanic saturation anomalies. Other researchers have identified chemical/microbial degradation processes for loss of CH_3Br in soils (Rice et al. 1996; Connell et al. 1997; Ou et al. 1997).

The behavior of methyl halides in freshwater systems has been much less studied. The goal of the present study was to measure the seasonal variation of CH_3Cl and CH_3Br in a freshwater lake (Lake Washington) and, using a simple steady-state box model, estimate the magnitudes of freshwater sources and sinks of these climatically important trace gases.

Measurements

Lake Washington is a monomictic, mesotrophic lake bordering Seattle, Washington (Fig. 1). The lake has a surface area of ~87 km^2, a maximum depth of 65 m, and a mean depth of ~33 m. Major feeder streams include the Cedar River (~57% by volume) and the Sammamish River (~27%), supplemented by a few small creeks (total 5–10%) and by precipitation (5–10%). About 75% of this flow comes during the rainy season (November–April), and the average turnover time (lake volume/input flux) of the whole lake is about 2.5 yr (METRO 1999). The only outlet is through Lake Union and Ballard Locks to Puget Sound. The vertical temperature structure in the lake is nearly uniform in winter at ~8°C (Fig. 2). Seasonal warming during spring and summer causes strong vertical stratification to develop in the upper water column. The highest surface temperatures (~23°C) occur in August in the upper ~10-m layer of the lake. Below this warm, summer, mixed layer is a strong thermocline, with the deeper waters ($z > 30$ m) remaining near 8°C throughout the year (Fig. 2). The average wind speeds over the lake are fairly constant throughout the year (~2.7 m s^{-1}) and slightly higher in early spring and autumn. Methyl halides were measured at a station located at the deepest region of the lake (*see Fig. 1*); at this site, physical, chemical, and biological measurements of Lake Washington have been made nearly continuously for more than 30 yr (Edmondson 1991).

Samples were collected from a small motor boat. Air samples were collected in stainless steel 1.5-L canisters and pressurized to 25 psi with a small, battery-driven pump (KNF Neuberger, Inc., Model UN05AT1). Water samples were collected using Niskin or Van Dorn bottles, then subsampled into 100-ml glass syringes. Vertical temperature profiles were measured by CTD (Seabird 9+) or Kahl digital thermometer. Samples were processed and analyzed within 24 h after collection. A purge-and-trap preconcentration method (after Bullister and Weiss 1988) was used to extract the dissolved methyl halides from the water sample and concentrate them on a cold trap, consisting of Porasil C and Porapak T held at dry ice temperatures. The contents of the cold trap were then heated rapidly and injected into a Hewlett Packard

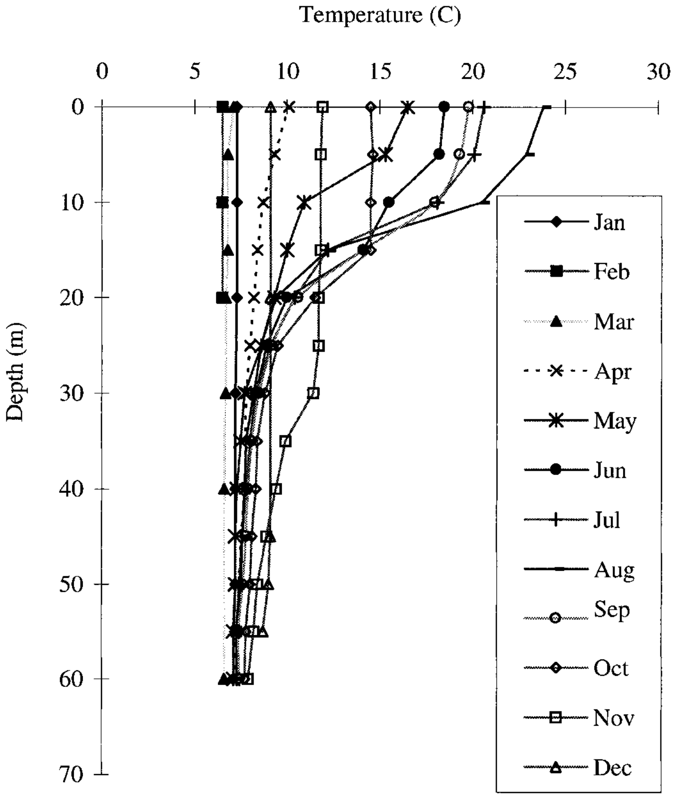

Fig. 2. Vertical profiles of monthly average temperature in Lake Washington, January–December 1997.

5890 Series II gas chromatograph. Final separation was done on a capillary column (DB-624 type, 75-m main column, 35-m precolumn). The compounds were detected using an electron capture detector (ECD). A 0.4% oxygen-doped nitrogen makeup gas was used to improve the sensitivity of the ECD to methyl halides, especially methyl chloride (Grimsrud and Miller 1978; Grimsrud 1993; Bu 1995). Working standards used for the water and air measurements were stored in high-pressure gas cylinders and calibrated at the Climate Monitoring and Diagnostics Laboratory (Lobert et al. 1996).

Data analysis

The atmospheric measurements of CH_3Cl and CH_3Br made during the study period (Table 1) have mean values of 596 ± 19 pptv (CH_3Cl) and 11.2 ± 0.3 pptv (CH_3Br), in good agreement with reported background mean values in the Northern Hemisphere (Lobert et al. 1996; Khalil and Rasmussen 1998).

Examples of vertical profiles of dissolved methyl halides measured in late winter (12 March 1998), spring (18 May 1998), and summer (31 July 1997) and vertical profiles of CFC-11 measured in winter (12 March 1998) and summer (20 August 1997) are shown in Fig. 3. Relative saturation factors (rsf) are calculated from the following equation for a general gas Z.

Table 1. Air measurements on Lake Washington.*

Date	CH_3Cl (pptv)	CH_3Br (pptv)
23 Aug 1995	596(12)	10.7(1.5)
17 Jul 1996	663(47)†	11.1(0.6)
31 Jul 1997	571(7)	11.5(0.7)
26 Feb 1998	602(5)	11.5(0.4)
12 Mar 1998	616(7)	11.3(0.3)
Average	596(19)	11.2(0.3)
Reported	591(60)‡	11.0(1.2)§

* Uncertainty is given by 1 standard deviation (1σ) in parentheses.
† Not included when calculating the average.
‡ CH_3Cl value is the average atmospheric concentration in the Northern Hemisphere, midlatitude, from Khalil and Rasmussen (1998).
§ CH_3Br value is the average atmospheric concentration in the Northern Hemisphere, marine background, from Lobert et al. (1996).

$$\mathrm{rsf} = \frac{[Z]}{[Z]_{eq}} = \frac{[Z]}{([Z]_{air}Hs)}$$

[Z] is the measured dissolved gas concentration in water (pM), $[Z]_{air}$ is the air concentration (pptv), Hs is the temperature-dependent Henry's Law solubility coefficient, as measured by De Bruyn and Saltzman (1997*a*) for methyl bromide and Eliot and Rowland (1995) for methyl chloride. $[Z]_{air}Hs$ gives the concentration at equilibrium $[Z]_{eq}$, and the relative saturation factor is the ratio of measured concentra-

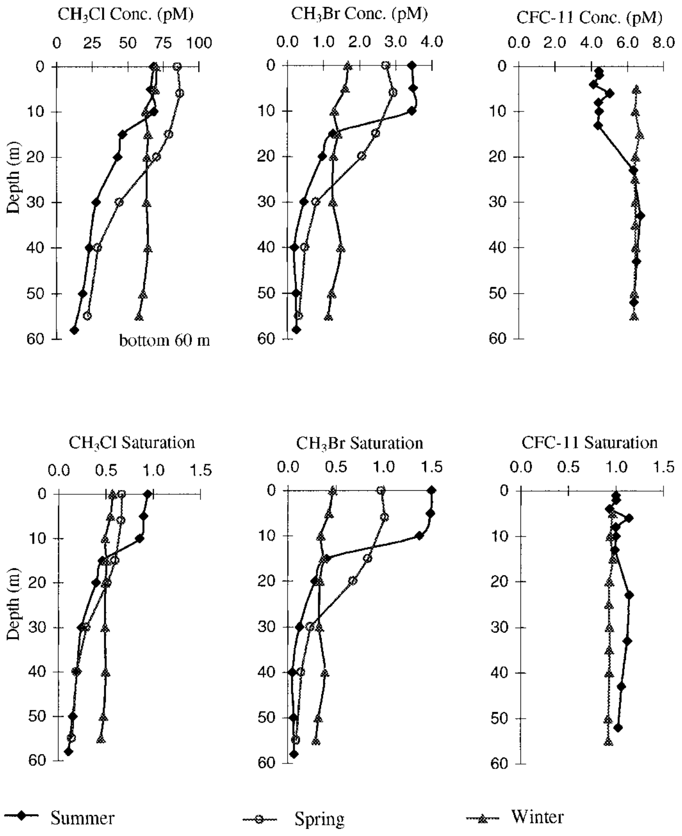

Fig. 3. Vertical profiles of methyl halides and CFC-11 in Lake Washington.

Table 2. Water measurements in Lake Washington.*

			Methyl halide concentration			
			Summer mixed layer		Summer deep water	
Year	Winter $[CH_3X]$ (pM)	rsf	$[CH_3X]$ (pM)	rsf	$[CH_3X]$ (pM)	rsf
CH_3Cl						
1998	63.9(3.7)	0.50(0.04)				
1997			67.6(1.2)	0.90(0.04)	20.5(6.5)	0.17(0.06)
1996			62.8(3.9)	0.70(0.02)	17.7(5.3)	0.13(0.04)
1995			68.5(4.8)	0.93(0.07)	21.6(9.3)	0.18(0.08)
Average	63.9(3.7)	0.50(0.04)	66.3(4.1)	0.84(0.12)	19.9(6.8)	0.16(0.06)
CH_3Br						
1998	1.36(0.18)	0.36(0.05)				
1997			3.43(0.05)	1.44(0.06)	0.28(0.12)	0.07(0.03)
1996			2.38(0.06)	1.01(0.06)	0.23(0.09)	0.06(0.03)
1995			4.24(0.69)	2.02(0.33)	0.88(0.19)	0.24(0.05)
Average	1.36(0.18)	0.36(0.05)	3.36(0.88)	1.50(0.47)	0.42(0.31)	0.12(0.09)

* Uncertainty is given by 1σ in parentheses.

tion to the concentration at equilibrium. Average methyl halide concentrations and corresponding rsf in the surface and deep layers in summer and winter over the study period are given in Table 2.

The wintertime CH_3X profiles (March 1998) show that both compounds are substantially undersaturated (rsf = 0.50 ± 0.04 for CH_3Cl, rsf = 0.36 ± 0.05 for CH_3Br) and vertically well-mixed throughout the water column (Fig. 3). In contrast, the summer profiles of the methyl halides have the maximum in the mixed layer with rsf = 0.84 ± 0.12 for CH_3Cl and rsf = 1.50 ± 0.47 for CH_3Br, decreasing quasi-exponentially to much lower values in the deeper waters of the lake ($z > 30$ m).

Because the observed winter profiles of CH_3Cl and CH_3Br in the lake are nearly constant with depth, we first model the wintertime lake as a single, well-mixed box in steady-state. Hence, for either methyl halide

$$\frac{dC}{dt} = \sum \text{sources} + \sum \text{sinks} = 0, \qquad (1)$$

where dC/dt is the rate of change of the methyl halide concentration (pmol d^{-1}) in the well-mixed box, Σ sources is the sum of individual source terms, and Σ sinks is the sum of individual sink terms.

Equation 1 can be rewritten with the individual source/sink component terms specified.

$$\frac{dC}{dt} = \mathrm{P} + \mathrm{J} + \mathrm{H} + \mathrm{E} + \mathrm{S} = 0 \qquad (2)$$

P is the rate of increase of dissolved methyl halide concentration due to unspecified in situ biological/chemical production processes, J is the rate of decrease of dissolved methyl halide concentration due to unspecified in situ biological/chemical consumption processes, H is the rate of decrease of dissolved methyl halide concentration due to hydrolysis, E is the rate of change of dissolved methyl halide concentration due to gas exchange, and S is the rate of change of dissolved methyl halide concentration due to halide substitution reactions. The E and S terms can act as either sources or sinks in the model.

Because both CH_3Cl and CH_3Br are undersaturated in winter, air–water gas exchange produces a net source term for both gases in the wintertime model.

$$\mathrm{E} = \frac{\mathrm{K_w}}{z_{\mathrm{mix}}}([\mathrm{CH_3X}] - [\mathrm{CH_3X}]_{\mathrm{eq}}) \qquad (3)$$

K_w is the gas exchange coefficient (m d^{-1}), z_{mix} is the thickness of the box (m), $[CH_3X]$ is the dissolved methyl halide concentration in the well-mixed box, and $[CH_3X]_{eq}$ is the equilibrium methyl halide concentration based on the atmospheric concentration of the gas and temperature-dependent Henry's Law coefficient.

Estimates of K_w for lakes have been made by Wanninkhof (1992).

$$\mathrm{K_w} = \mathrm{a}v^{1.64}\left(\frac{\mathrm{Sc}}{660}\right)^{-1/2} \qquad (4)$$

a is 0.42 (based on lake studies by Wanninkhof [1992]), v is the mean wind speed (the annual average of 2.7 m s^{-1} is used in this study), and Sc is the nondimensional Schmidt number for the gas.

An expression for the temperature-dependent Schmidt number for CH_3Br in water is given by De Bruyn and Saltzman (1997*b*).

$$\mathrm{Sc} = \frac{\mu}{D} = 2004 - (93.5T) + 1.39T^2 \qquad (5)$$

μ is the kinetic viscosity of water, D is the molecular diffusivity of the dissolved gas, and T is the water temperature (°C). Estimates of the Schmidt number for CH_3Cl can be made based on the D values for CH_3Cl and CH_3Br using the additive method of Reid (1987).

The dominant chemical sink term for the methyl halides is in situ hydrolysis (H) via the reaction

$$\mathrm{CH_3X} + \mathrm{H_2O} \rightarrow \mathrm{CH_3OH} + \mathrm{H^+} + \mathrm{X^-}. \qquad (6)$$

Table 3. Lake Washington model results.*

	E (pM d^{-1})	H (pM d^{-1})	(P+J)† (pM d^{-1})	P‡ (pM d^{-1})	J§ (pM d^{-1})	[CH$_3$X] (pM)	[CH$_3$X]$_{eq}$ (pM)	K$_w$ (m d^{-1})	τ (d^{-1})
Winter: steady-state, single-box model; layer thickness (z_{mix}) = 33 m									
CH_3Cl	+2.940	−0.010	−2.840	0	−2.840	63.9	127.80	1.52	22
CH_3Br	+0.110	−0.005	−0.105	0	−0.105	1.36	3.78	1.50	12
Summer: steady-state box model; upper mixed layer (Z_{max}) = 11 m									
CH_3Cl	+2.428	−0.069	−2.359	+6.161	−8.520	66.3	78.90	2.12	8
CH_3Br	−0.213	−0.079	+0.292	+0.607	−0.315	3.36	2.24	2.09	5

* +, production; −, consumption.

† Term balance of E+H.

‡ Difference of (P+J)−J; P is assumed 0 in winter.

§ Difference of (P+J)−P; J values in summer are assumed to be 3 times greater than J in winter.

This reaction is first order with respect to dissolved methyl halide concentration

$$H = k_{H_2O}[CH_3X], \tag{7}$$

where k_{H_2O} is the first-order temperature-dependent chemical loss rate coefficient for the methyl halide (Eliot and Rowland 1995).

There is also the possibility of gain or loss due to the halide substitution reaction

$$CH_3Br + Cl^- \rightarrow CH_3Cl + Br^-, \tag{8}$$

which acts both as a source term for CH_3Cl and a sink term for CH_3Br. The rate of this substitution reaction is first order in [Cl$^-$]; however, the measured [Cl$^-$] in Lake Washington is less than 10^{-4} M (our determination by ion chromatography), compared to ~0.56 M for [Cl$^-$] in seawater. Although the concentration changes due to halide substitution (S) are quite important in assessing methyl halide balances in marine environments, they are negligible in this freshwater environment ($<$0.1% relative to the gas exchange, E, or hydrolysis, H, terms in Lake Washington).

Because the residence time for water in Lake Washington is relatively long (approximately 2.5 yr or a daily water exchange of only ~1/900 by volume), we also neglect any contribution from inflowing streams or precipitation to the methyl halide mass balance on the timescales (a few weeks) appropriate to our steady-state assumption.

In the freshwater lake model, the halide substitution term (S) is considered negligible, so from Eq. 2, assuming steady state for each methyl halide, the air–sea exchange term E is balanced by the net of remaining in situ terms.

$$E = -(P + J + H) \tag{9}$$

The results from the steady-state single-box model are listed in Table 3. The hydrolysis terms (H) at wintertime temperatures are small relative to the calculated air–water exchange terms (E). The net sum of (P + J) is negative for both CH_3Cl and CH_3Br in the winter steady-state single-box model.

Because the steady-state turnover timescale is defined as the reservoir divided by the sum of the sinks (or the sum of sources), it is necessary to try to estimate the in situ production (P) and consumption (J) components of the net (P + J) separately. Assuming that CH_3Cl production is related to phytoplankton growth and is negligible in winter (because of strong mixing and deepening of the mixed layer and low light levels) and that J is related to respiration, which is less sensitive to these factors, then in winter, P = 0 and J = −2.84 pM d^{-1} for CH_3Cl (Table 3). In the same way, assuming that P = 0 for CH_3Br in winter, then J = −0.105 pM d^{-1}.

The model indicates that Lake Washington is a significant net sink for methyl halides in winter. The net of all the in situ production (or consumption) terms in the box model corresponds to an in situ loss rate of ~−4 to −5% d^{-1} (CH_3Cl) and ~−7 to −9% d^{-1} (CH_3Br), with corresponding apparent turnover times $\tau = 22 \pm 3$ d for CH_3Cl and $\tau = 12 \pm 2$ d (CH_3Br) at the mean wintertime lake temperature (~8°C). These uncertainties (1σ) have been estimated by a Monte Carlo approach (Diaconis and Effron 1983; Huang 1999).

As the upper layer of the lake warms from spring into summer (Fig. 2), the vertical distributions of dissolved methyl halides undergo significant changes (Fig. 3). In the summertime surface mixed layer, the relative saturation factors for CH_3Cl and CH_3Br are observed to be much higher than in winter. The CH_3Cl mixed layer concentration increases only slightly over winter levels; nearly all of the increase in relative saturation (from rsf = 0.50 ± 0.04 in winter to rsf = 0.84 ± 0.12 in summer) is due to the decreased CH_3Cl solubility at the higher summer water temperatures. For CH_3Br, the concentrations in summer were more than double the winter values and, together with the summer warming of the surface waters, dramatically increased the surface saturation factor from rsf = 0.36 ± 0.05 (winter) to rsf = 1.50 ± 0.47 (summer). The increase in CH_3Br concentration in the summer mixed layer and strong supersaturation imply a net in situ production in this season.

The vertical density stratification in the lake is very strong in summer and essentially absent in winter. In summer, a sharp thermocline separates a warm, ~11-m-thick near-surface mixed layer from the colder, isothermal deeper waters, which remain near 8°C year-round (Fig. 2). During this summer season, the lake may then be modeled as a simple two-layer system, with a thick (~50 m), deep box isolated from the thin, near-surface layer, which can freely exchange gases with the overlying atmosphere. Mass exchange through eddy diffusion between the two layers in this strongly stratified system is shown to be minimal in summer, as follows. The diffusive length scale L is given by

$$L = (K_z t)^{0.5}, \tag{10}$$

where K_z is the eddy diffusion coefficient (cm^2 s^{-1}), and t is time (s).

Based on estimates of $K_z = 0.02$ cm^2 s^{-1} for the summer thermocline of Lake Washington (Quay et al. 1980, 1986), the effective scale length for eddy diffusion during the entire 4-month summer period is <5 m. Therefore, vertical diffusive exchange with the underlying thermocline is assumed to play a negligible role relative to rapid gas exchange and in situ production and consumption rates in altering the methyl halide content of the surface box during the summer season.

An independent estimate of the upper limit for the diffusion coefficient describing mixing across the summer thermocline of the stratified lake can be made using CFC-11, a conservative tracer in oxic waters. In winter, the vertical profile of dissolved CFC-11 is nearly uniform (Fig. 3) and maintained close to saturation equilibrium by rapid gas exchange with the atmosphere. As the upper layer of the lake warms in summer, the CFC-11 solubility decreases, and the concentration of dissolved CFC-11 in the upper mixed layer decreases because of gas exchange losses to the atmosphere (*see Fig. 3*). In contrast, the deep-water CFC concentration does not show significant change within the uncertainty of the measurements (±0.2 pM). The deep-lake CFC burden in summer can be maintained close to its wintertime value only if diffusive loss of CFC-11 from this deep layer to the surface mixed layer is very slight over this 5-month period (March to August). The minimal change in CFC-11 concentrations observed between winter and summer in the deep water (<0.2 pM) imply an upper limit to the value for the diffusion coefficient between the upper and deep layers corresponding to $K_z < 0.05$ cm^2 s^{-1}, consistent with the earlier estimates (Quay et al. 1980).

Therefore, for the steady-state box model in summer, the exchange of methyl halides between the surface and deep boxes is assumed to be negligible. Applying this steady-state model yields a daily upper (mixed) layer net rate for (P + J) of ~ -2.359 pM d^{-1} for CH_3Cl and ~ 0.292 pM d^{-1} for CH_3Br in summer.

Both production, P, and consumption, J, rates of CH_3Cl are likely much higher in summer than in winter because of the increased temperature and biological activity, but the difference between production and consumption rates in summer is not necessarily larger. In summer, the average temperature in the surface water is 12–15°C higher than in winter. As a general rule, temperature-dependent biochemical processes typically increase by a factor of 2–3 (or greater) for every 10°C increase in temperature. Making the conservative assumption that the J rate in summer is ~3 times that of J in winter, the P in summer can be roughly estimated for CH_3Cl in summer as

$$P + J = P + 3(-2.84) = -2.359 \qquad P = 6.161 \text{ pM d}^{-1}$$

and for CH_3Br in summer as

$$P + J = P + 3(-0.105) = 0.292 \qquad P = 0.607 \text{ pM d}^{-1}.$$

The apparent turnover timescale for CH_3Cl in summer is given by the reservoir divided by the sum of the summer sinks (or sources) in Table 3.

$$\tau_{CH_3Cl} = \frac{[CH_3Cl]}{(H_{CH_3Cl} + J_{CH_3Cl})} = \frac{[CH_3Cl]}{(E_{CH_3Cl} + P_{CH_3Cl})} \sim 8 \text{ d}$$

Applying the same crude approach to CH_3Br yields an estimated turnover time.

$$\tau_{CH_3Br} = \frac{[CH_3Br]}{(E_{CH_3Br} + H_{CH_3Br} + J_{CH_3Br})} = \frac{[CH_3Br]}{P_{CH_3Br}} \sim 5 \text{ d}$$

Notice that in both summer and winter the turnover time for CH_3Cl is approximately twice that for CH_3Br, though the turnover of both species is much more rapid in summertime than in wintertime. It is also interesting that this approach yields a molar ratio of production of $CH_3Cl:CH_3Br$ in this freshwater system of order 10 : 1, similar to that observed in laboratory cultures of marine phytoplankton (Scarratt and Moore 1998) and about one-half the average molar flux ratio (20 : 1) observed in coastal salt marshes (Rhew et al. 2000).

Samples were taken in summer 1997 and winter 1998 at different locations in Lake Washington to assess possible spatial variations of methyl halide distributions. Measurements were also made in source streams and in a feeder lake (Lake Sammamish) each summer during the study period. These studies show little variability in CH_3Cl distribution in this region but reveal evidence of possible anthropogenic input of CH_3Br. Results are discussed below and summarized in Tables 4 and 5.

Discussion

The results from this study indicate that Lake Washington is a sink for atmospheric CH_3Cl throughout the year, with a net air-to-water CH_3Cl flux into the lake in both summer and winter. In winter, the stratification of the lake breaks down because of vertical convection, resulting in a vertically homogeneous water column in both physical and chemical properties. In summer, the near-surface water warms and stratifies, leading to a two-layer system, with negligible exchange between the surface and deeper layers. Although the temperature in the deep layer is nearly constant throughout the year, the CH_3Cl concentrations in the deep layer decreases to low levels during summer, probably because of a combination of in situ chemical and biological removal processes and the isolation of this layer from exchange with near-surface water during this period. The decreases in methyl halide concentrations in the isolated deep box are consistent with the net in situ removal rates determined in the single-box (wintertime) model, indicating that the removal rates in the deep water do not vary dramatically on an annual cycle

The observed seasonal behavior of CH_3Br in the upper layer of the lake is distinctly different from that of CH_3Cl. The major undersaturation (rsf = 0.36 ± 0.05) in winter must be caused by in situ consumption, whereas the strong supersaturation (rsf = 1.50 ± 0.47) observed in the surface layer in summer, despite higher hydrolysis rates in the warmer water, indicates a rapid in situ production rate (~0.6 pM d^{-1}), corresponding to a replacement time in the mixed layer

Table 4. Summary of methyl halide measurements in Lake Washington's tributary rivers.*

Sample location	[CH_3Cl] (pM)			[CH3Br] (pM)		
	4 Aug 97	3 Sep 96	1 Aug 95	4 Aug 97	3 Sep 96	1 Aug 95
Bear Creek		51.5(0.50)	50.2(0.65)		1.91(0.71)	3.34(1.36)
Cedar River	67.6(0.83)	60.5(0.58)	65.8(0.85)	2.43(0.96)	2.40(0.89)	3.36(1.39)
Juanita Beach		30.9(0.30)	59.9(0.77)		0.79(0.30)	2.87(1.16)
Lewis	65.9(0.76)	35.4(0.35)	73.9(0.76)	1.61(0.59)	0.51(0.20)	2.57(0.95)
Lewis (pond)†		11.7(0.12)			8.76(3.36)	
Lewis downstream	36.2(0.43)			0.78(0.30)		
Lewis upstream	40.1(0.47)			0.97(0.37)		
May Creek			65.4(0.84)			3.36(1.28)
Mercer Creek			28.9(0.37)			2.82(1.16)
Sammamish (Marymoor)	49.5(0.76)		50.1(0.65)	2.72(1.29)		5.84(2.93)
Sammamish (T. Park)			50.9(0.66)			5.39(2.46)
Sammamish River	40.9(0.61)	58.1(0.56)		5.16(2.39)	4.03(1.50)	
Swamp Creek			32.2(0.41)			3.81(1.44)
Thornton Creek	51.1(0.60)	47.6(0.46)	53.4(0.69)	1.78(0.67)	1.62(0.60)	2.60(0.99)
Average of each year	50.2(0.64)	47.3(0.46)	53.1(0.68)	2.21(0.94)	1.88(0.70)	3.60(1.51)
Average of all		50.2(0.59)			2.56(1.05)	
SD		2.9(0.12)			0.91(0.42)	

* Relative saturation factor (rsf) is given in parentheses.
† Data from Lewis Pond is not included in the average calculation.

of less than 1 week. From winter to summer, the lake role changes from a net sink to a net source of CH_3Br. As for CH_3Cl, the CH_3Br concentrations in the deep water in summertime are much lower (close to the detection limit) than in winter, indicating a continuous removal after the winter season, which is well fit to an exponential decay at the observed wintertime loss rate.

The methyl halide concentrations are assumed to be in steady state in the upper layer of the water column in both winter and summer. In reality, the methyl halide concentrations in these boxes do undergo measurable changes during the transition from winter to summer conditions: the average concentrations of both species in the surface waters increases by 2 pM between the winter and summer (Table 2). If these concentration changes are assumed to occur at a constant rate during the ~4-month transition period between late winter (March) and summer (July), then the average rate of increase is ~0.02 pM d^{-1}, a small value relative to the other

Table 5. Methyl halide measurements in Lake Sammamish (L.Sam.) and Sammamish River (Sam.R.).*

Date	Sample location	CH_3Cl (pM)	CH_3Br† (pM)
Summer 1997			
6 Aug 97	Sta. 1 Issaquah Creek exit	54.3(0.89)	2.53(1.26)
6 Aug 97	Sta. 2 Lewis Creek exit	58.2(0.94)	2.44(1.20)
6 Aug 97	Sta. 3 middle L.Sam.	58.3(0.93)	2.27(1.11)
6 Aug 97	Sta. 4 middle L.Sam.	57.4(0.90)	2.22(1.07)
31 Jul 97	Idylwood–L.Sam.	57.3(0.86)	2.53(1.19)
6 Aug 97	Sta. 5 Sam.R. entrance	52.4(0.80)	2.94(1.40)
31 Jul 97	Turf Farm–L.Sam.	44.0(0.66)	3.70(1.73)
31 Jul 97	Boat Launch–L.Sam.	44.8(0.65)	4.10(1.87)
31 Jul 97	Log boom–L. Washington	50.7(0.79)	9.01(4.35)$^{-}$
31 Jul 97	L. Washington	68.3(0.94)	2.79(1.21)
Average		54.6(0.84)	2.84(1.34)
SD		7.1(0.11)	0.65(0.28)
Winter 1998			
26 Feb 98	Juanita Beach	77.2(0.60)	1.96(0.52)
26 Feb 98	Kenmore boat launch	80.1(0.26)	2.39(0.62)
26 Feb 98	Logboom County park	79.5(0.61)	2.19(0.56)
Average		78.9(0.61)	2.18(0.57)
SD		1.5(0.01)	0.21(0.05)

* Relative saturation factor (rsf) is given in parentheses.
† Average and standard deviation does not include this value $^{-}$.

leading terms in the summertime mass balance model (Table 3). Therefore, the steady-state assumption should not lead to significant errors in calculating the in situ terms.

These patterns for methyl halide distributions in freshwater are distinctly different from those observed in the sea. The open ocean is a net source of CH_3Cl except in high-latitude cold waters (Khalil et al. 1998) and is a net sink for CH_3Br everywhere, except in coastal water and upwelling zones (Lobert et al. 1995; Moore and Webb 1996). Differences in the phytoplankton and microbial species in fresh versus marine environments may be responsible. Some marine algae are known to produce CH_3Cl (Wuosmaa and Hager 1990), which could account for the general supersaturations observed in the near-surface ocean. It is possible that particular freshwater species might be sources contributing to the CH_3Br supersaturations observed in Lake Washington in summer. Nonbiological processes, such as chloride substitution, also contribute to the differing saturation states in fresh versus marine systems.

Based on our preliminary measurements in Lake Washington, one can make an order-of-magnitude estimate of the role of freshwaters in the global methyl halide budgets by assuming that all fresh lakes in the world are similar to Lake Washington. The total area of freshwater lakes is 8.25×10^5 km^2, approximately 0.28% of the ocean area. If the observed mean rates of flux of CH_3Cl into Lake Washington are taken as the global mean freshwater rate, then the annual global sink would be $\sim$1 Gg yr^{-1}, a completely insignificant sink relative to the 3,000 Gg global annual flux (Khalil and Rassmussen 1998). Lake Washington acts as a source of CH_3Br in summer and a sink in winter, and it is likely that the net annual flux is small. Even if we assume the freshwaters act only as a source or sink throughout the year, this overestimate of the annual global freshwater CH_3Br flux would fall into the range of -0.1 Gg (consumption) to $+0.06$ Gg (production). This value is likewise completely negligible compared to the estimated global annual production of 141 Gg (Lobert et al. 1996).

The two most important rivers entering Lake Washington (Cedar River and Sammamish River) were measured each summer from 1995–1997 to see how the methyl halide distributions in the lake might be affected by input from the major source waters (Table 4). The Cedar River, which flows swiftly from a protected watershed through rural forested areas of minimal development, was found to be consistently undersaturated for CH_3Cl in each of the three summer samplings (rsf $=$ 0.83, 0.58, 0.85) and closer to saturation equilibrium for CH_3Br (rsf $=$ 0.96, 0.89, 1.39). The Sammamish River, which meanders slowly through more developed agricultural and residential areas between Lake Sammamish and Lake Washington, was found to be undersaturated in CH_3Cl in all sample locations over 3 yr (rsf $=$ 0.56–0.76), but strongly supersaturated in CH_3Br (rsf $=$ 1.29–2.6). Other small feeder creeks were also sampled for completeness but are less important because of their small contribution to the inflow to Lake Washington. The concentration in these small streams was variable, but all showed consistent CH_3Cl undersaturation, and most showed CH_3Br undersaturation as well. The highest supersaturations for CH_3Br were observed in Lewis Pond, which stored the water drained from a building construction site, and in the Sammamish River, which was consistently supersaturated every time it was measured. Both of these cases suggest that human activities may have affected CH_3Br concentrations in local waters.

After the Sammamish River was found to have high levels of CH_3Br, another survey of Lake Sammamish and a few other sampling points downstream along the Sammamish River was made the following summer 1997 (Table 5). Lake Sammamish was found to be undersaturated for CH_3Cl (rsf $= 0.84 \pm 0.11$), but again supersaturated for CH_3Br (rsf $= 1.34 \pm 0.28$). These numbers agreed very well with the Lake Washington summer surface data, suggesting similar chemical or biological processes throughout the watershed. Along the Sammamish River, methyl halide concentrations and saturation factors are similar to those found in Lake Washington at all sampling sites except Log Boom Park, where CH_3Cl was typical (rsf $=$ 0.79) but CH_3Br had a saturation factor as high as rsf $=$ 4.35. The cause of the extremely high supersaturation is not clear, but may be related to local algae blooms in this shallow and warm end of the lake, nearby human activities (lumber yard, concrete/gravel business, Kenmore air harbor, golf course, combined storm-sewer outfall), or both.

Even though a number of different processes may be involved in the production and consumption of these compounds in Lake Washington, the observed $CH_3Cl : CH_3Br$ ratio (15–25) was relatively constant over the study period and much lower than the corresponding marine value 50–500 (Huang 1999). This low ratio in freshwater may be related to the high concentrations of Cl^- in seawater and the enhanced importance of Cl^- substitution reaction in converting CH_3Br to CH_3Cl in marine environments. Biological processes, which differ in fresh- and seawater, may also contribute to the different $CH_3Cl : CH_3Br$ ratios observed.

Very few studies have been made of the biological processes involving methyl halides in freshwater. Goodwin (1996) and Goodwin et al. (1997) reported a high rate of CH_3Br degradation by bacterial oxidation in a warm-water lake. More research is needed to investigate the possible biological sources and sinks of methyl halides, the mechanisms for the production and consumption of these compounds in fresh/seawater, and the importance of these terms in the methyl halide budgets in these environments.

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