



## Dynamics of CFCs in northern temperate lakes and adjacent groundwater

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[1] Three dimictic lakes and one meromictic lake in and near the Trout Lake, Wisconsin, watershed were sampled to determine the variation of chlorofluorocarbon (CFC) concentrations within the lakes. The lakes were sampled during stratified conditions, during fall turnover, and during ice cover. The results demonstrate a considerable variation in CFC concentrations and corresponding atmospheric mixing ratios in the lakes sampled, both with depth and season within a given lake, and across different lakes. CFC profiles and observed degradation were not related to the groundwater inflow rate and hence are likely the result of in-lake processes influenced by CFC degradation in the (lake) water column, CFC degradation in the lake-bed sediments, and gas exchange rates and the duration of turnover (turnover efficiency).

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### 1. Introduction

[2] Since the early 1990s, chlorofluorocarbons (CFCs) have been used as a practical and cost-effective means to trace the movement and determine the recharge date of relatively young groundwater [Plummer and Busenberg, 2000]. In general, most of the studies utilizing CFCs have involved precipitation infiltrating the groundwater system through relatively thin unsaturated zones [e.g., Busenberg and Plummer, 1992; Cook *et al.*, 1995]. CFCs have not been as widely used in settings where surface waters are important sources of recharge to the groundwater system. Groundwater recharge from a lake is different than recharge through the unsaturated zone because dynamics in the lake can potentially confound the input time series of CFC concentrations. The difference could be especially prominent in lake systems with large fluctuations of temperature and deep anoxic zones. There have been a few studies involving recharge of surface waters into groundwater systems, but the CFC tracing and dating techniques used for traditional recharge systems could be applied because the surface-water residence times were relatively short and there was little variation in surface temperature [e.g., Katz *et al.*, 1995; Plummer *et al.*, 1998a, 1998b]. In other cases, where the recharge occurs through organic-rich sediments and anoxic conditions, the CFCs can become degraded, resulting in an estimated groundwater recharge date that is older than the true date [e.g., Cook *et al.*, 1995; Plummer *et al.*, 1998a, 1998b]. Other potential issues with the use of CFCs include problems with dating extremely young waters [Hunt *et al.*, 2005], issues with mixing of waters of varying age [Goode, 1996; Bethke and Johnson, 2002a, 2002b; Weissman *et al.*, 2002], and the leveling off or declining input curves [Plummer and Busenberg, 2000].

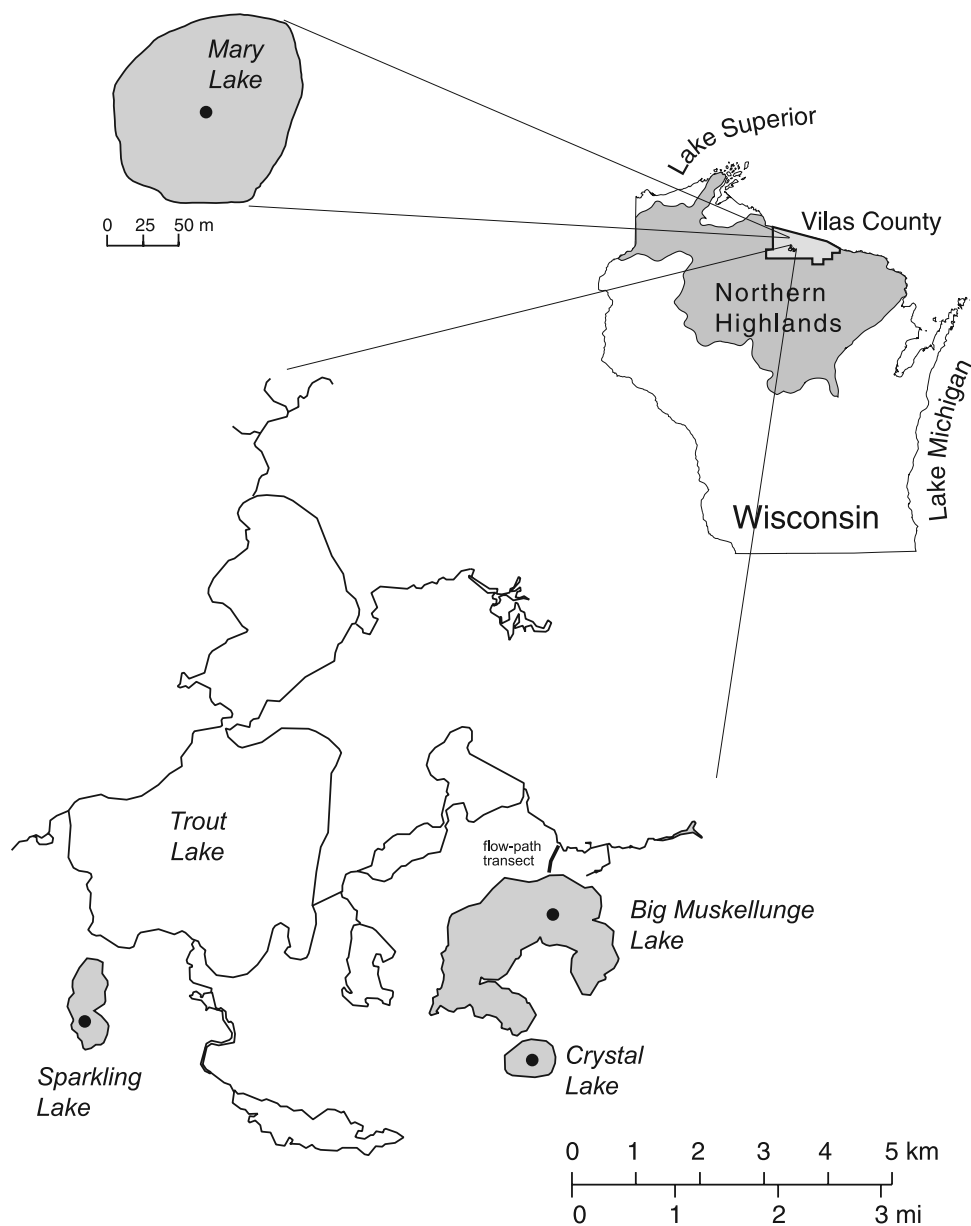
[3] The Trout Lake Water, Energy and Biogeochemical Budgets (WEBB) project is currently investigating groundwater/surface water interactions and processes controlling the geochemistry of small headwater streams in the Trout Lake watershed (Figure 1) through a combination of numerical modeling and sampling along piezometer nest transects [Walker and Bullen, 2000]. Groundwater in the watershed is recharged through one of three sources: (1) unsaturated-zone recharge, (2) lake-derived recharge, or (3) wetland-derived recharge. Because the solute composition and associated mineral weathering of these three sources can differ dramatically [Bullen *et al.*, 1996; Masbruch, 2005], it is important to follow the flow path from each source separately. Information on travel times between two points along a known flow path can be used to constrain the velocities through the subsurface, improving our understanding of model calibration [Pint *et al.*, 2003] and mineral weathering rates.

[4] The purpose of this paper is to investigate the feasibility of CFCs to date groundwater derived from lakes. The study design looked at interlake and intralake variability over a period extending from September (stratified conditions) to March (ice-covered conditions). The lakes studied included (1) three dimictic lakes (lakes that are characterized by complete mixing during fall and spring turnover) that spanned a gradient of groundwater inflow, and (2) one meromictic lake (a lake that does not commonly turn over). In addition, the groundwater downgradient of the losing shore of one of the study lakes was sampled for CFCs to quantify groundwater recharge dates. The results of this study have application to any temperate lake system or groundwater system dated with CFCs if lakes are an important source for recharge.

### 2. Study Area

[5] The Trout Lake watershed is in the Northern Highlands geographic province of Wisconsin. Detailed descriptions of the watershed and lakes are given elsewhere

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**Figure 1.** Map showing the location of the study lakes.

[Magnuson *et al.*, 1984; Elder *et al.*, 1992] and will be summarized here. The 118-km<sup>2</sup> watershed consists of low-relief glacial terrain set in 30–50 m of relatively uniform outwash sand. Because of the highly conductive nature of the outwash sand and the low relief, streamflow is dominated by groundwater; there is very little direct surface runoff. None of the lakes sampled in this study has surface inlets or outlets. The watershed is heavily forested with a history of selective logging. Precipitation averages 79 cm/yr [Cheng and Anderson, 1994], and recharge to the groundwater system averages about 27 cm/yr [Hunt *et al.*, 1998]; because direct surface runoff is minimal, evapotranspiration and canopy interception combined average about 52 cm/yr.

[6] Three of the National Science Foundation Long-Term Ecological Research (LTER) study seepage lakes were selected for this study: Big Muskellunge, Crystal, and Sparkling lakes. Each of these lakes is dimictic, undergoing complete mixing through thermal turnover twice each year

(fall and spring). A fourth lake near the Trout Lake watershed (Mary Lake) was also selected as an extreme case, as it is a meromictic lake that rarely mixes through thermal turnover. Sheltering due to topography and trees along the shore are thought to be the cause of the meromixis condition. Physical and chemical characteristics of the study lakes are summarized in Table 1 (T. K. Kratz and E. H. Stanley, Physical and Chemical Limnology, National Science Foundation North Temperate Lakes LTER program, <http://www.limnology.wisc.edu>, Center for Limnology, University of Wisconsin-Madison). Direct precipitation is the dominant source of water to the lakes, and all three LTER lakes are near circumneutral, fairly dilute in solutes, and relatively deep (18–22 m). Groundwater inflows for three of the four lakes were determined quantitatively using water isotopes [Krabbenhoft *et al.*, 1994], and ranged from relatively high groundwater inflow (Sparkling Lake) to low groundwater inflow (Crystal Lake). Mary Lake has an unknown

**Table 1.** Physical and Selected Chemical Characteristics of the Four Study Lakes

	Crystal	Big Muskellunge	Sparkling	Mary
Area, ha	36.7	396.3	64	13.3
Mean depth, m	10.4	7.5	10.9	8.6
Maximum depth, m	20.4	21.3	20	21.7
Mean residence time, years	10	7.5	11	9
Ice-on date <sup>a</sup>	21 Dec 1998	23 Dec 1998	22 Dec 1998	...
Ice-off date <sup>b</sup>	15 Apr 1999	16 Apr 1999	9 Apr 1999	...
pH	6	7.3	7.3	...
ANC, $\mu\text{eq/L}$	16	366	612	...
Conductivity, $\mu\text{S/cm}$	14	49	80	60
Total P, $\mu\text{g/L}$	8.6	22.5	15.2	...
Total N, $\mu\text{g/L}$	207	489	375	...
SiO <sub>2</sub> , $\mu\text{g/L}$	20	145	3582	...
Secchi depth, m	7.3	6.7	6.1	...
Groundwater inflow, <sup>c</sup> $\text{cm/yr}$	7	15	29	...

<sup>a</sup>Ice-on is the date when the lake is completely frozen.

<sup>b</sup>Ice-off is the date when the lake is completely free of ice.

<sup>c</sup>Rates as reported by *Krabbenhoft et al.* [1994].

groundwater exchange. Lakes in the area are generally ice covered for 5 months each year. For the year studied, the ice-on date occurred somewhat later than normal (third week of December instead of mid-November). The ice-off date was fairly typical for the area (second to third week of April).

### 3. Methods

#### 3.1. Sample Collection

[7] The three dimictic lakes in the Trout Lake watershed were sampled at the location of the deep hole at three different times to determine the variability of CFC concentration within a lake. The lakes were sampled during stratified conditions (September 1998), during fall turnover (November 1998), and during ice cover (March 1999). Samples were also collected from the deep hole of the meromictic lake during the same sampling periods. In most cases, samples were collected near the surface and just above the sediment interface. For Mary Lake a more detailed depth profile was collected during the November sampling. For Big Muskellunge Lake, detailed profiles were collected during the fall and spring sampling periods. Littoral zone pore water and well nests were sampled once during August 1996 along a transect from Big Muskellunge Lake to Allequash Creek (flow path transect, Figure 1).

[8] CFC samples were collected and analyzed using procedures described by *Busenberg and Plummer* [1992]. In addition to CFCs, dissolved gases (argon, carbon dioxide, methane, nitrogen, and oxygen) were collected and analyzed for most surface-water samples and selected groundwater samples using procedures developed the U.S. Geological Survey (E. Busenberg, personal communication, 1997). Samples were collected in duplicate or triplicate for surface-water samples and in sets of five for groundwater samples. Replicates were analyzed for most samples collected. In almost all cases the reproducibility between replicates was within 5%; thus the average is reported in this paper. The analytical accuracy for CFC-11 and CFC-12 is typically less than 2% of the reported value. For CFC-113, the accuracy is about 3%.

[9] Depth profiles of temperature, dissolved oxygen, pH, and specific conductance were collected using a Hydrolab multiparameter water-quality sonde and data logger (the use

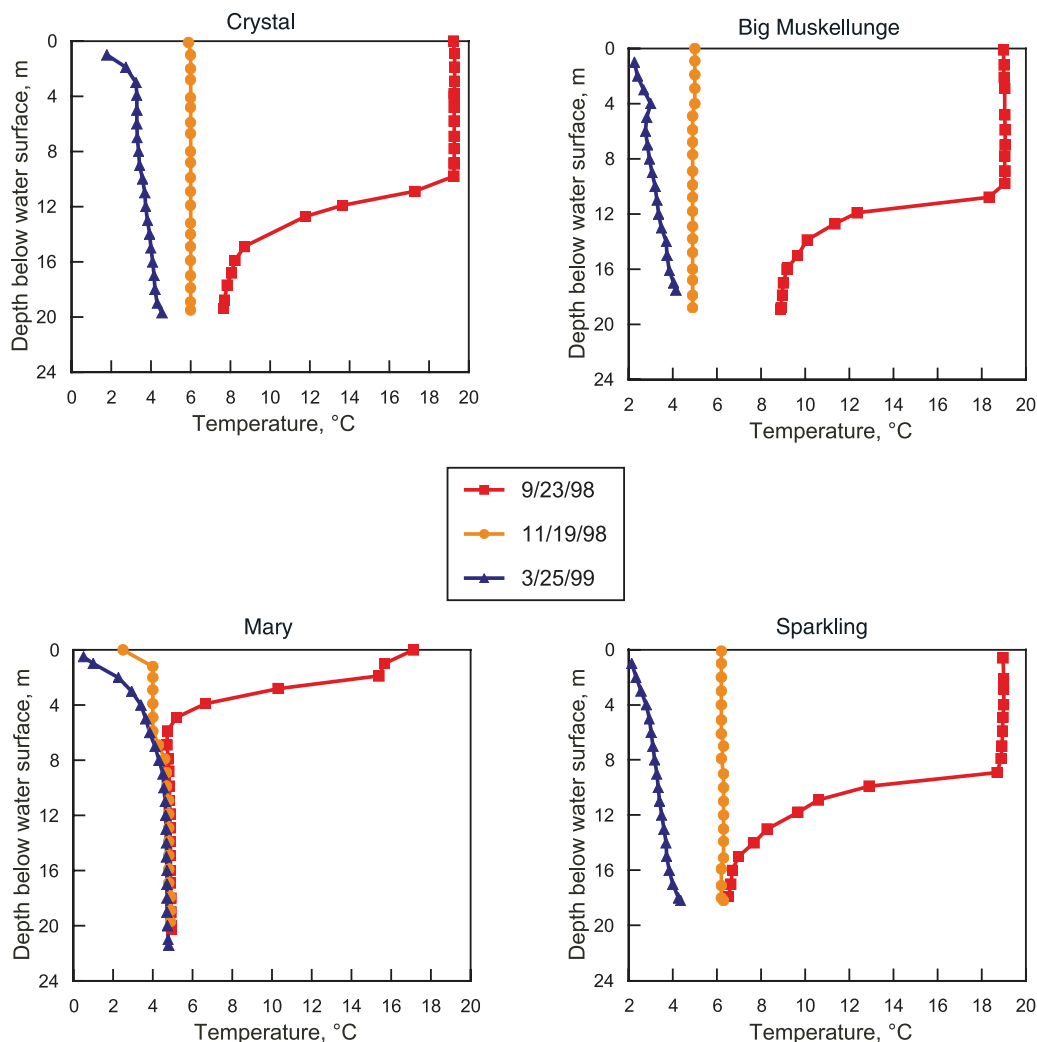
of trade names in this publication is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey). The unit was calibrated each morning prior to deployment in the field. Calibrations for pH were accomplished using two standards bracketing the range expected for the day. A single specific conductance standard was used for calibration. Dissolved oxygen was calibrated using an air-equilibration procedure. New dissolved-oxygen membranes were installed prior to each sampling trip. Depths for the profiles were determined using the depth sensor contained within the Hydrolab sonde.

[10] Samples for oxygen-isotope analysis were collected in glass bottles and were unfiltered and untreated. Analyses of oxygen isotopes were performed at the U.S. Geological Survey National Research Program Laboratory in Menlo Park, California. Oxygen-18 values were measured using CO<sub>2</sub>-H<sub>2</sub>O equilibration [*Epstein and Mayeda*, 1953] on a Finnigan-Mat 251 mass spectrometer, and are reported in standard delta notation relative to Vienna standard mean ocean water (VSMOW).

[11] The three main sources of water in the Allequash Creek watershed [*Walker et al.*, 2003] are meteoric water that recharges through the ground surface (unsaturated-zone recharge, average  $\delta^{18}\text{O}$  value of approximately  $-11.3\text{‰}$ ), evaporatively fractionated water from lakes that reenters the groundwater system through the lake bed (lake recharge,  $\delta^{18}\text{O}$  ranging from  $-4.4$  to  $-5.5\text{‰}$ ), and water that recharges the aquifer from wetlands (intermediate  $\delta^{18}\text{O}$  resulting from variable evaporative fractionation of meteoric water that has short residence time on the wetland surface). In general, deuterium (D) and oxygen-18 ( $^{18}\text{O}$ ) values are needed to distinguish between different sources of water; however, since the meteoric water in the surface and subsurface waters exhibits a narrow range of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values due to mixing of the seasonal meteoric signal [*Walker and Krabbenhoft*, 1998] and because lakes in the region tend to have well-averaged water isotope compositions [*Krabbenhoft et al.*, 1990, 1994], subsequent discussion will rely on the value for  $\delta^{18}\text{O}$  alone to discriminate the water source.

#### 3.2. Dating Methods

[12] The general procedure of dating groundwater using CFCs is based on Henry's law solubility, and will be



**Figure 2.** Temperature profiles with depth for the four study lakes. Note that lakes are arranged according to the amount of groundwater inflow received by the lake, starting with low input (Crystal Lake, upper left) and increasing in a clockwise direction (Big Muskellunge Lake, then Sparkling Lake). The groundwater input to Mary Lake is unknown.

summarized here (a detailed description is given by *Plummer and Busenberg* [2000]). The equilibrium solubility of a particular CFC in water is given through Henry's law as

$$C_i = x_i K_{Hi} (P - p_{H_2O}), \quad (1)$$

where  $C_i$  is the concentration of the  $i$ th CFC in water,  $K_{Hi}$  is the Henry's law constant for the  $i$ th CFC,  $x_i$  is the dry air mole fraction of the  $i$ th CFC,  $P$  is atmospheric pressure, and  $p_{H_2O}$  is the vapor pressure of water. The Henry's law constant is a function of temperature and salinity, although for freshwater systems the salinity effects are negligible. The water vapor pressure is also a function of temperature, and atmospheric pressure is assumed to be a general pressure based on elevation. For traditional groundwater recharge through a relatively thin unsaturated zone, the concentration of a particular CFC when it reaches the water table is determined by the temperature at the water table during recharge, and the dry air mole fraction at the time of recharge. An apparent date of recharge can be determined by solving equation (1) for  $x_i$  and using the time history of

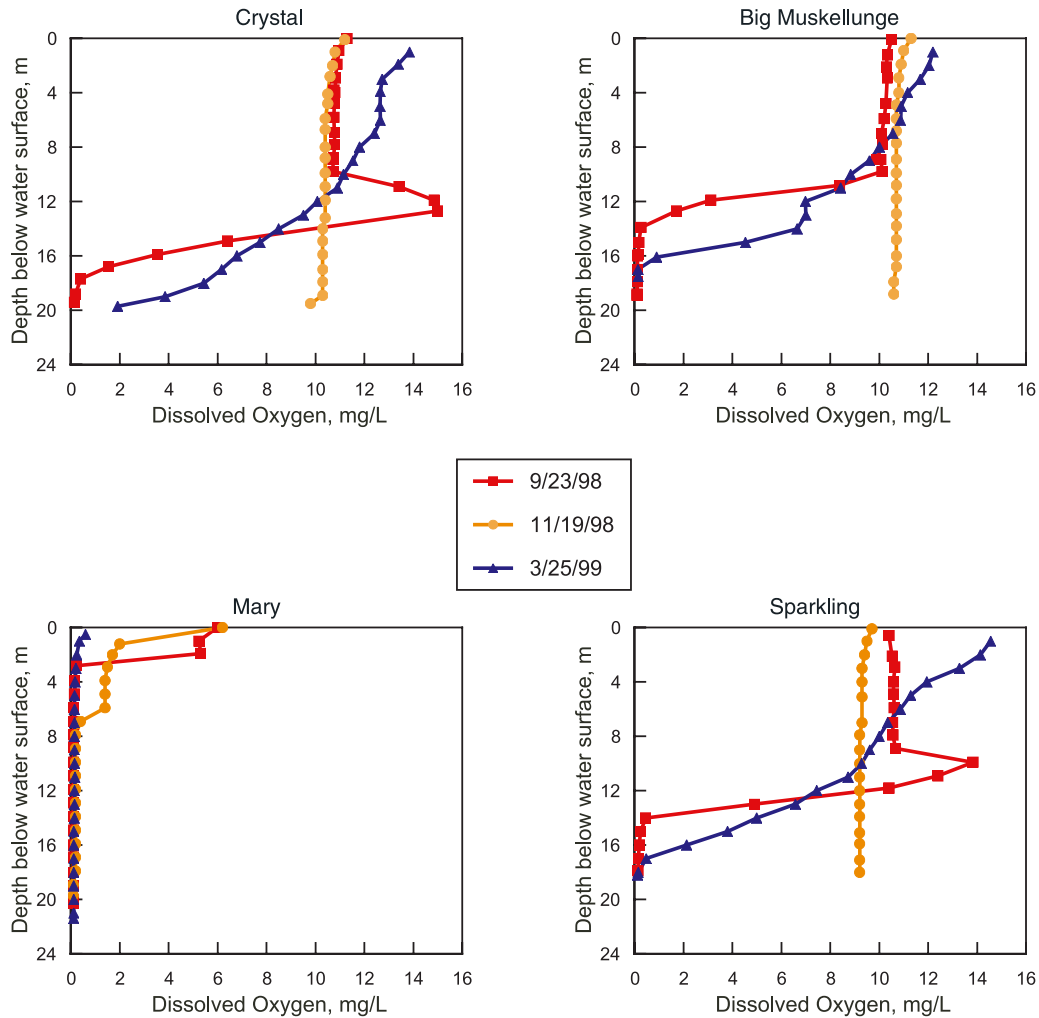
atmospheric CFC concentrations to yield the date (where the atmospheric mixing ratio equals the dry air mole fraction). Accurate estimates of recharge temperature are critical to solving equation (1) because they influence both the Henry's law constant and the vapor pressure of water.

[13] Generally for traditional recharge the average annual air temperature provides a reasonable estimate of recharge temperature. However, for recharge occurring through lakes, the lake temperature can be highly variable, especially in the littoral zone. Noble gases and  $N_2$  solubilities have been widely used as indicators of recharge-water temperature [*Busenberg et al.*, 1993]. Applying Henry's law to measured argon and nitrogen aqueous concentrations (if denitrification is minimal) can provide estimates of water temperature at the time of last contact with the atmosphere.

## 4. Results and Discussion

### 4.1. Field-Measured Lake Profiles

[14] Depth profiles showing temperature distributions for the four study lakes are shown in Figure 2. The three dimictic lakes show a typical pattern for a northern temperate climatic



**Figure 3.** Dissolved-oxygen profiles with depth for the four study lakes.

setting: A strong stratification exists in September, prior to freezing in November the thermal stratification breaks down and is mixed, and during ice cover in March weak thermal stratification occurs. At the September sampling, the depth to the thermocline (thus the extent of the well-mixed layer, or epilimnion) is roughly 10 m for all three lakes. For the meromictic lake (Mary Lake), the thermocline in September is shallow, and the November sample exhibits weak stratification. The uniformity of temperature at depth for all three Mary Lake profiles is evidence that the entire lake did not mix. However, there is evidence that the shallow portion of the lake (less than about 6–8 m depth) did mix.

[15] Dissolved-oxygen profiles for the four study lakes are shown in Figure 3. As with temperature, the dissolved-oxygen profiles for the three dimictic lakes show a typical pattern for the study area: During stratification in September the epilimnion remains oxygenated, after fall turnover in November the entire profile is uniformly oxygenated, and during ice cover in March the epilimnion remains oxygenated. Below the thermocline the dissolved-oxygen concentration quickly goes to zero, and the lower portion of the lake (hypolimnion) becomes anoxic. Methane is also noted in the hypolimnion, reflecting the reduced conditions (Table 2). The sharp increase in dissolved oxygen near the thermocline in Crystal and Sparkling lakes is indicative of a positive heterograde [Cole, 1979]. This condition occurs in clear

lakes where light penetrates the thermocline allowing phytoplankton to thrive. Oxygen accumulates because photosynthesis exceeds respiration and turbulent mixing is low at these greater depths.

#### 4.2. CFC-11 in Lakes

[16] The CFC-11 results, expressed in terms of atmospheric mixing ratios, are plotted with depth in Figure 4 and listed in Table 3. Note that modern air (1998) for CFC-11 corresponds to 267 pptv (plus or minus 2%). The atmospheric mixing ratios for the three dimictic lakes vary significantly with depth and season within a lake and between lakes. In September, only the surface sample from Crystal Lake was near equilibrium with the atmospheric CFC-11 atmospheric mixing ratio. Of the surface samples from the other dimictic lakes, Big Muskellunge had CFC-11 atmospheric mixing ratios below atmospheric levels and Sparkling Lake was above atmospheric levels. After the fall turnover event, the surface and deep lake CFC-11 concentrations were nearly identical, which would indicate the complete mixing of the lake (Figure 4, November sampling). However, the resulting CFC-11 atmospheric mixing ratios were less than atmospheric levels, indicating the entire lake volume did not reach equilibrium for any of the dimictic lakes. Temporal variations within the uppermost sample reflect the effects of mixing efficiency within the lake and

**Table 2.** Dissolved-Gas Data and Estimated Recharge Temperatures

Site	Field Temperature	N <sub>2</sub> , mg/L	Ar, mg/L	O <sub>2</sub> , mg/L	CO <sub>2</sub> , mg/L	CH <sub>4</sub> , mg/L	Excess N <sub>2</sub> , mg/L	Estimated Recharge Temperature, °C	Excess Air, cm <sup>3</sup> /L at STP
Aug 1996									
Well P1-10a	12.6	15.5	0.55	0.09	12.67	0.003	0.76	17.3	-0.01
Well M-50	13.2	18.8	0.67	6.19	0.85	0.000	0.97	8.3	0.00
Well P1-10b	11.8	18.3	0.65	0.58	6.46	0.516	1.03	9.8	0.00
Well P1-70a	10.0	17.6	0.68	0.04	2.56	2.285		7.9	-0.34
Sep 1998									
Big Musky, 3.0 m	19.0	16.6	0.60	7.14	2.44	0.000		14.9	1.13
Big Musky, 6.4 m	19.0	14.3	0.53	6.31	2.69	0.000		19.4	0.10
Big Musky, 15.8 m	9.0	19.1	0.72	0.00	16.57	1.002		5.9	0.34
Big Musky, 18.3 m	8.9	19.0	0.71	0.00	17.57	1.938		6.4	0.41
Crystal Lake, 4.6 m	19.3	14.2	0.53	7.60	0.90	0.002		18.9	-0.18
Crystal Lake, 18.3 m	7.7	19.4	0.74	0.14	12.76	0.130		4.7	0.10
Mary Lake, 10.0 m	4.8	22.6 <sup>a</sup>	0.87 <sup>a</sup>	0.00 <sup>a</sup>	92.86 <sup>a</sup>	>15		-1.3	0.20 <sup>b</sup>
Mary Lake, 2.0 m	15.4	14.9	0.56	0.05	10.60	0.000		16.8	-0.06
Sparkling Lake, 4.6 m	19.0	14.3	0.53	7.39	1.20	0.004		18.9	-0.03
Sparkling Lake, 16.8 m	6.5	18.7	0.72	0.00	17.09	4.080		5.8	-0.11
Nov 1998									
Mary Lake, 0.3 m	2.4	18.7	0.71	0.06	16.08	0.000		6.7	0.30
Mary Lake, 0.3 m	2.4	18.8	0.71	0.06	15.99	0.000		6.4	0.26
Mary Lake, 3.7 m	4.0	18.8	0.71	0.06	15.86	0.001		6.2	0.16
Mary Lake, 3.7 m	4.0	19.9	0.73	0.06	16.20	0.000		6.6	1.47
Mary Lake, 9.8 m	4.7	26.6 <sup>a</sup>	0.99 <sup>a</sup>	0.04 <sup>a</sup>	105.9 <sup>a</sup>	>15		-5.1	1.67 <sup>b</sup>
Mary Lake, 9.8 m	4.7	27.0 <sup>a</sup>	1.00 <sup>a</sup>	0.05 <sup>a</sup>	109.8 <sup>a</sup>	>15		-5.4	1.83 <sup>b</sup>
Mary Lake, 17.4 m	4.8	29.4 <sup>a</sup>	1.10 <sup>a</sup>	0.00 <sup>a</sup>	163.2 <sup>a</sup>	>15		-8.3	1.91 <sup>b</sup>
Mary Lake, 17.4 m	4.8	30.2 <sup>a</sup>	1.12 <sup>a</sup>	0.00 <sup>a</sup>	164.2 <sup>a</sup>	>15		-8.9	2.30 <sup>b</sup>
Mar 1999									
Big Musky, 3.0 m	2.7	20.5	0.79	11.03	2.74	0.000		2.3	0.02
Big Musky, 3.0 m	2.7	20.6	0.79	9.60	4.07	0.000		2.0	-0.01
Big Musky, 10.1 m	3.2	20.7	0.79	7.54	6.41	0.001		2.4	0.29
Big Musky, 14.9 m	3.7	20.6	0.78	5.03	9.18	0.002		2.5	0.18
Big Musky, 14.9 m	3.7	20.8	0.79	4.54	9.74	0.002		2.2	0.28

<sup>a</sup>Analytical interference due to excessive CH<sub>4</sub> levels; results have higher uncertainty.

<sup>b</sup>Highly degraded water. Recharge temperature not accurate.

atmospheric exchange; these effects will be discussed in detail in the fall turnover section to follow.

[17] For samples below the thermocline, the CFC-11 atmospheric mixing ratios in September are much lower than the reset value after fall turnover (November), indicating that considerable degradation during stratification is likely. Because the lakes are commonly anoxic at depth, degradation processes are consistent with previous observations of CFC behavior in anoxic conditions [Bullister and Lee, 1995; Oster et al., 1996; Plummer et al., 1998a, 1998b; Aeschbach-Hertig et al., 2002]. For the meromictic lake, the CFC-11 at depth is completely depleted, presumably because values in the hypolimnion are rarely reset through turnover, and thus the anoxic degradation processes occur for a longer period of time. It is conceivable that the groundwater inflow might be altering the CFC profiles by contributing older (thus lower CFC) water to the lake. We do not believe this is the case, however, because the profiles from the lake with the highest groundwater inflow (Sparkling) are remarkably similar to the lake with lowest groundwater inflow (Crystal). Thus we conclude that CFC-11 is a poor tracer for lake-derived groundwater recharge due to its susceptibility to anoxic degradation. For this reason, the remaining discussion will focus on CFC-12.

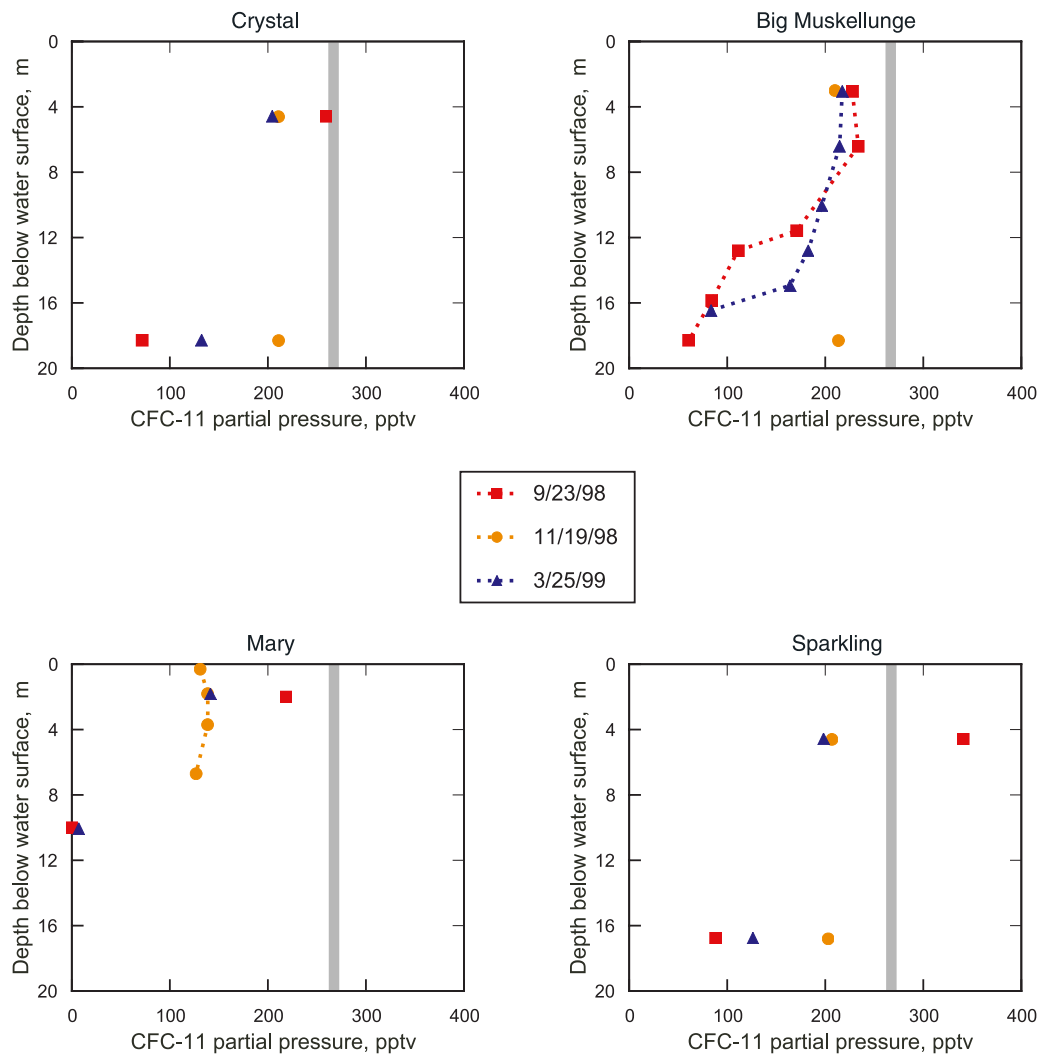
### 4.3. CFC-12 in Lakes

[18] The CFC-12 results, expressed in terms of atmospheric mixing ratios, are plotted with depth in Figure 5. For CFC-12, modern air (1998) corresponds to 537 pptv (plus

or minus 2%). Similar to the CFC-11 profiles, there is a considerable variation with depth and season, both within a given lake and between lakes. Therefore discussion of CFC-12 results is presented by season.

#### 4.3.1. Stratification (September 1998)

[19] CFC-12 atmospheric mixing ratios in the epilimnion (above the thermocline) of two of the dimictic lakes (Crystal and Big Muskellunge) were at or near equilibrium with atmospheric concentrations during late-summer stratification as indicated by the September samples. Similar to CFC-11, Sparkling Lake concentrations of CFC-12 exceeded equilibrium with the atmosphere for unknown reasons. Thus, in general, CFC-12 values indicate that the shallow zone of the dimictic lakes contain fairly "equilibrated" water that would be expected from gas exchange rates. Using the CFC-12 values from Crystal and Big Muskellunge Lakes along with observed lake temperature, the apparent recharge date of water infiltrated from the shallow zone of these dimictic lakes during stratification ranges from 1991 to 1994. Clearly, direct application of the observed mixing ratios would be misleading, as the CFC values are influenced by the efficiency of atmospheric equilibration. CFC-12 values in the shallow zone of Mary Lake (a meromictic lake) were undersaturated with respect to modern air. This discrepancy is likely a result of some degradation of CFC-12 similar to CFC-11, as evidenced by the anoxic zone of Mary Lake being fairly shallow during September (about 3 m).



**Figure 4.** CFC-11 expressed as atmospheric mixing ratios plotted against depth of sample collection for the four study lakes. The shaded region represents the range of mixing ratios corresponding to modern air (1998).

[20] During September, CFC-12 values in the dimictic lakes were slightly higher in the epilimnion than the hypolimnion (Figure 5). We believe this is a result of not reaching complete equilibrium with the atmosphere during the previous spring turnover and partial degradation in the anoxic reducing conditions below the thermocline. The presence of anoxic degradation is supported by the larger declines with depth in the CFC-11 September profiles (Figure 4).

[21] CFC-12 atmospheric mixing ratios in the deep zone of the meromictic lake also appear to be degraded (Figure 5) based on the anoxic conditions that predominate (Figure 3), as evidenced by comparing the CFC-11 profile (Figure 4) with the CFC-12 profile (Figure 5).

#### 4.3.2. Fall Turnover (November 1998)

[22] In the three dimictic lakes, shallow CFC values were variable relative to atmospheric mixing ratios during stratification. However, CFC values in the deep zones were typically higher during fall turnover than summer stratification largely due to mixing and temporary exposure of the entire water body to the atmosphere. The field parameter

profiles collected during fall turnover indicate that the dimictic lakes were thoroughly mixed; however, the CFC-12 values were similar in the shallow and deep zones of each lake, indicating less than complete mixing with regard to CFCs. During fall turnover, anoxic zones were not present in the dimictic lakes (Figure 3), and the degraded water at depth is exposed to the atmosphere and mixed with the surface water, which has an atmospheric mixing ratio approaching modern 1998 water. CFC values throughout Big Muskellunge Lake were essentially in equilibrium with the atmosphere during fall turnover. Results from duplicate samples for the shallow and deep samples in Big Muskellunge Lake indicate an anomalously high combined sampling and analytical uncertainty of nearly  $\pm 50$  pptv; thus both values could be considered to be in equilibrium with the atmosphere. Shallow and deep samples collected from Crystal and Sparkling lakes had similar values but were somewhat below equilibrium with the atmosphere (Figure 5). These results indicate that lake morphology likely plays an important role in the level of lake-atmosphere equilibration of CFCs during turnover.

**Table 3.** CFC-11 and CFC-12 Concentrations and Atmospheric Mixing Ratios

Site	Recharge Temperature	CFC-11		CFC-12	
		Concentration, pg/kg	Mixing Ratio, pptv	Concentration, pg/kg	Mixing Ratio, pptv
Sep 1998					
Crystal Lake, 4.6 m	19.3	435.1	259.3	217.0	538.5
Crystal Lake, 18.3 m	4.7	263.3	71.6	324.8	399.4
Big Musky, 3.0 m	19.4	380.5	227.8	205.5	511.9
Big Musky, 6.4 m	19.4	390.6	233.8	205.2	511.1
Big Musky, 11.6 m	14.0	372.5	171.1	265.4	521.6
Big Musky, 12.8 m	10.0	300.0	111.2	353.2	572.9
Big Musky, 15.8 m	6.0	286.2	84.2	385.9	509.0
Big Musky, 18.3 m	6.0	206.6	60.8	354.8	468.0
Mary Lake, 2.0 m	16.8	412.7	218.3	212.8	474.5
Mary Lake, 10.0 m	4.8	0.7	0.2	115.8	143.2
Sparkling Lake, 4.6 m	18.9	583.0	340.7	240.4	586.0
Sparkling Lake, 16.8 m	5.8	303.0	88.0	356.1	464.4
Nov 1998					
Crystal Lake, 4.6 m	6.0	716.4	376.3	210.8	496.6
Crystal Lake, 18.3 m	6.0	716.7	365.2	210.9	482.0
Big Musky, 3.0 m	4.9	762.9	426.8	210.0	530.6
Big Musky, 18.3 m	4.9	775.1	443.7	213.4	551.7
Mary Lake, 0.3 m	2.4	556.1	332.7	130.9	359.5
Mary Lake, 1.8 m	4.0	531.6	326	138.4	385.7
Mary Lake, 3.6 m	4.0	531.2	332.2	138.3	393.0
Mary Lake, 6.7 m	4.1	483.5	328.3	126.7	390.5
Mary Lake, 9.8 m	4.7		113.6		139.7
Mary Lake, 13.7 m	4.8		60.5		74.8
Mary Lake, 17.4 m	4.8		68.8		85.0
Sparkling Lake, 4.6 m	6.2	694.4	357.5	206.8	476.9
Sparkling Lake, 16.8 m	6.2	681.6	346.4	203.0	462.1
Mar 1999					
Crystal Lake, 4.6 m	2.4	868.5	450.5	204.4	486.8
Crystal Lake, 18.3 m	2.4	562.3	404.5	132.3	437.1
Big Musky, 3.0 m	2.4	923.7	488.1	217.4	527.5
Big Musky, 6.4 m	2.4	911.2	500.4	214.5	540.7
Big Musky, 10.1 m	2.4	835.5	531.4	196.7	574.3
Big Musky, 12.8 m	2.4	776.0	481.0	182.6	519.8
Big Musky, 14.9 m	2.4	698.0	460.5	164.3	497.7
Big Musky, 16.5 m	2.4	355.2	422.6	83.6	456.7
Mary Lake, 1.8 m	2.4	600.9	373.5	141.4	403.7
Mary Lake, 10.0 m	2.4	30.1	167.2	7.1	180.7
Sparkling Lake, 4.6 m	2.4	842.5	471.2	198.3	509.2
Sparkling Lake, 16.8 m	2.4	536.2	391.3	126.2	422.9

[23] The ability to “reset” the lake water to equilibrium with atmospheric concentrations is expected to be greater in Big Muskellunge Lake than in Crystal or Sparkling lakes due to two factors. First, the larger mean depths (volume divided by surface area) of Crystal and Sparkling lakes (10.4 and 10.9 m, respectively) limit their ability to expose the entire lake to the atmosphere during the time between turnover and ice cover. Big Muskellunge Lake, on the other hand, has a much smaller mean depth (7.5 m) than Crystal and Sparkling lakes. Second, the percent of CFC-depleted water is smaller in Big Muskellunge Lake because the relative volume below the thermocline is less. While all three dimictic lakes are approximately 20 m deep and all develop thermoclines at about 12 m below the surface, the volume of water below the thermocline of Crystal and Sparkling lakes during summer stratification was about 20% of the total lake volume, compared with about 9% for Big Muskellunge Lake. As a result, there is relatively less depleted CFC-12 water in the initial mixed water in Big Muskellunge Lake.

[24] Another factor contributing to the CFC values below equilibrium with the atmosphere concerns the equilibration process at the air-water interface and the kinetics of the

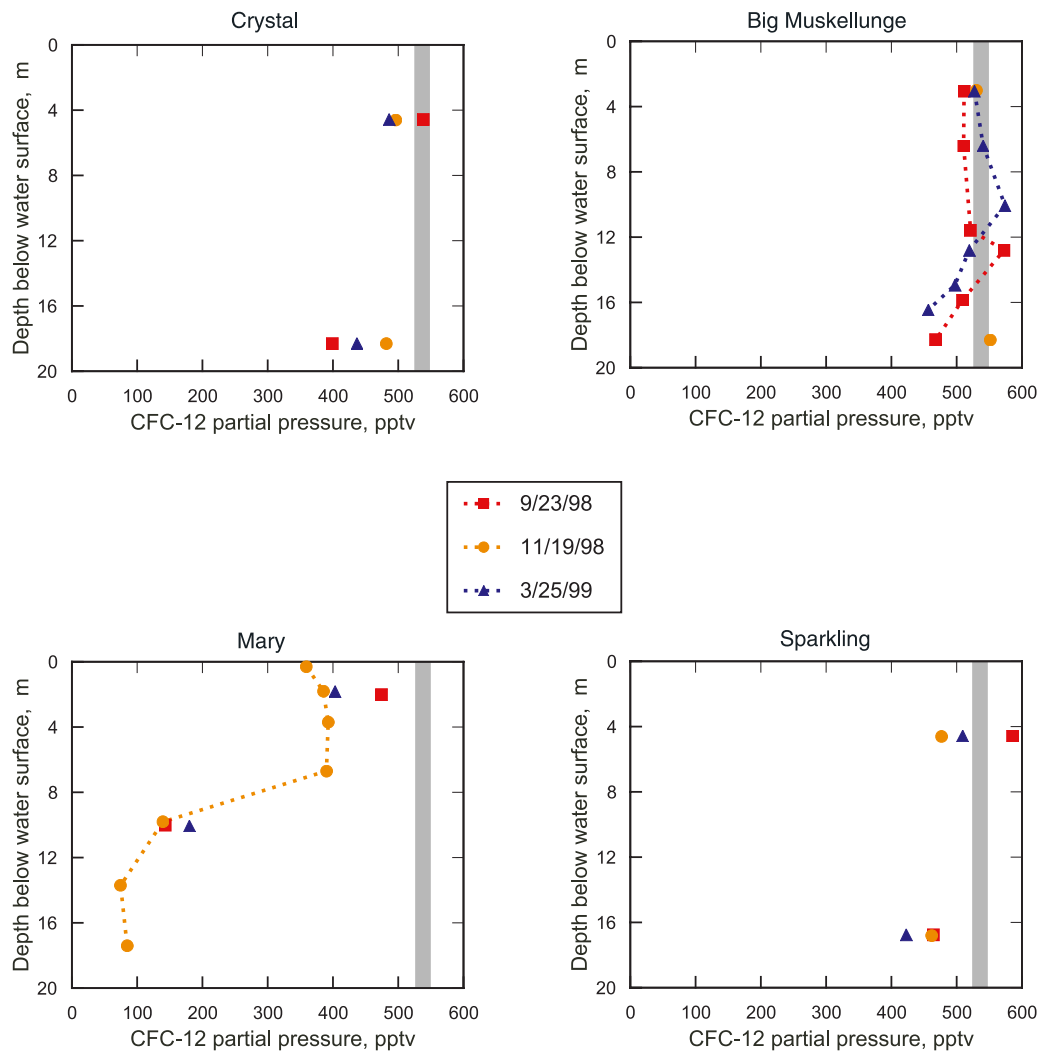
mixing process in the epilimnion. For the study lakes, the piston velocities may be of the order of 0.5 m/d [Cole and Caraco, 1998]. With a 12-m-thick epilimnion, it would take roughly 24 days to come to equilibrium with the atmosphere. In the fall as temperatures drop rapidly and in the spring with quickly increasing temperatures, the gas concentrations could differ substantially from equilibrium.

[25] During fall turnover the shallow water (<7 m) in Mary Lake had CFC-12 values at the surface that were somewhat lower than in September (Figure 5), suggesting the mixolimnion water of Mary Lake did partially mix with the monimolimnion water during November 1998. This can also be observed in Figures 2 and 4. CFCs remained highly degraded in the deep zone of Mary Lake, however, and were appreciably below equilibrium concentrations, indicating that the zone of mixing did not extend to deeper lake water.

#### 4.3.3. Ice Cover (March 1999)

[26] March CFC-12 values in the epilimnion are similar to the values in November. Assuming the ice cover completely removes contact with the atmosphere, one would expect the surface samples to be roughly the same in November and March. Because the November sample was taken roughly a month before complete ice cover, it is likely that the slightly





**Figure 5.** CFC-12 expressed as atmospheric mixing ratios plotted against depth of sample collection for the four study lakes. The shaded region represents the range of mixing ratios corresponding to modern air (1998).

higher values in March at the surface are the result of continued mixing and interaction with the atmosphere prior to ice cover as the lakes cooled. The shallow water in Big Muskellunge Lake continued to have higher CFC-12 values than Crystal or Sparkling lakes, which is consistent with the influence of lake morphometry described earlier. Ice cover CFC-12 values in the shallow zone of Big Muskellunge Lake represents near-equilibrium conditions that existed during turnover and immediately prior to first ice cover. For Crystal and Sparkling lakes, CFC-12 values in the shallow zone during ice cover were below equilibrium. Atmospheric mixing ratios for these two lakes were similar to those measured in fall turnover samples and may be indicative of a lesser ability of these lakes to “reset.”

[27] CFC-12 values in the deep zone of Big Muskellunge Lake were lower than at fall turnover; this coincides with an anoxic zone that had developed (Figure 3), indicating likely anoxic degradation. This is supported by the steep decline measured in the Big Muskellunge Lake CFC-11 profile (Figure 4) in the deeper lake water. A deep anoxic zone was observed in Sparkling Lake and was not observed in Crystal Lake during the March sampling (Figure 3), although

dissolved oxygen rapidly decreased with depth in Crystal Lake. Accordingly, CFC-12 values in the deep zones of Crystal and Sparkling lakes were slightly less than those measured in the deep zone of Big Muskellunge Lake (Figure 5). It is likely that the lower deep atmospheric mixing ratios in Crystal and Sparkling lakes are a combination of anoxic degradation and the inability of these lakes to reach atmospheric equilibration.

[28] Shallow anoxia during ice cover was an important control of CFCs in the meromictic lake (Mary Lake). Whereas during November the three dimictic lakes had somewhat similar CFC-12 values compared with the shallow meromictic lake (Figure 5), CFC-12 values in the shallow zone of Mary Lake were considerably lower than the dimictic lakes after ice cover. The shallow zone of Mary Lake was more reducing than the dimictic lakes during this period (Figure 3), and thus we conclude that anoxic degradation similar to that observed in deep anoxic zone in Big Muskellunge Lake was occurring throughout the water column at Mary Lake.

[29] On the basis of the premise that interaction with the atmosphere is negligible during ice cover, it is possible to

**Table 4.** CFC-11 and CFC-12 Recharge Dates for Groundwater Samples Collected at the WEBB Site

Site	$\delta^{18}\text{O},\%$	CFC-11			CFC-12		
		Concentration, pg/kg	Apparent Recharge		Concentration, pg/kg	Apparent Recharge	
			Littoral or Terrestrial	Deep Lake		Littoral or Terrestrial	Deep Lake
Well P1-05a	-4.9	5.17	1952–1954	n/a	148	1972–1984	n/a
Well P1-10a	-5.0	3.13	1950–1953	1953–1956	14.3	1954–1960	1956–1957
Well P1-10b	-5.2	1.85	1950–1952	1952–1955	102	1968–1977	1970–1972
Well P1-10c	-5.3	2.36	1950–1952	1952–1955	24.8	1958–1964	1960–1961
Well P1-30	-5.7	8.32	1953–1956	1956–1962	25.3	1958–1964	1960–1962
Well P1-70a	-6.8	3.42	1950–1953	1953–1957	14.1	1954–1960	1956–1957
Well P1-70b	-5.3	16.1	1955–1960	1960–1966	11.1	1952–1958	1954–1956
Well M-36	-6.3	3.29	1950–1953	1953–1956	4.86	1948–1953	1949–1950
Well M-50	-11.3	340	1976	n/a	134	1974	n/a

estimate rates of degradation using the March sampling. Assuming the samples near the surface represent completely mixed conditions as the ice cover formed, and presuming minimal mixing in the epilimnion during stratified conditions under the ice cover, the difference between the deep and surface concentrations represents an estimate of the amount of degradation that has occurred at depth. Using the time between ice-on and the sample date as the time interval, one can compute first-order rates of degradation for the four lakes. Using the minimum and maximum concentrations from the duplicate samples, a range of degradation rates was determined. For CFC-11, the first-order degradation rates for Crystal, Big Muskellunge, Mary and Sparkling lakes are 1.6–1.8, 3.7–3.9, 9.8–15.7, and 1.7–1.9 yr<sup>-1</sup>, respectively. For CFC-12, the degradation rates for Crystal, Big Muskellunge, Mary and Sparkling lakes are 0.3–0.5, 0.5–0.7, 2.7–3.9, and 0.5–1.0 yr<sup>-1</sup>, respectively. These rates agree fairly well with values reported previously [Bullister and Lee, 1995]. As expected, the degradation rates are much higher for CFC-11 than for CFC-12. The ratio of the degradation rates for CFC-11 to CFC-12 range from 2 to 8, which is in the range of values previously reported [Plummer and Busenberg, 2000; Oster et al., 1996; Cook et al., 1995].

#### 4.4. Dating Lake-Derived Groundwater

[30] Recharge to the groundwater system from lakes can be expected to occur in both the shallow littoral zones near the shore and the deeper profundal portion of a lake. For recharge occurring in the littoral zones, the recharge concentration will depend on the surface temperature, which can vary substantially over the year (as much as 20°C in the study area), and potential degradation of CFC as the water travels through organic-rich/anoxic lake bed sediments. In the deeper portions of the lake, the initial CFC-12 concentration at depth prior to recharge depends on the time when water leaves the lake (since there is a difference in deep lake CFC concentration over time in dimictic lakes) and amount of degradation due to anoxic conditions. Both temperature and anoxia-induced artifacts in lake CFCs may confound attempts to interpret CFC concentrations measured in lake-derived groundwater in both space (shallow versus deep lake source area) and time. To clarify the importance of these potentially confounding influences, we used two simple models of recharge to estimate apparent recharge dates using the CFC data.

[31] Walker and Krabbenhoft [1998] have shown that naturally occurring isotopes of water (<sup>18</sup>O, D) are powerful discriminators between recharge originating from the unsaturated zone and lakes. More specifically, the  $\delta^{18}\text{O}$  composition of Big Muskellunge Lake water is generally of the order of -5‰, and unsaturated-zone recharge is generally of the order of -11.3‰. Using this distinction, we determined that all but one of the samples collected along a transect from Big Muskellunge Lake to Allequash Creek (Table 4) is composed of water that is recharged from the lake.

[32] For terrestrial recharge we used an average air temperature of 10°C as the recharge temperature. For water recharging from the littoral zone of the lake, we estimated a range of dates using recharge temperatures ranging from 2.4°–20°C, which corresponds to the usual range in temperature of the surface of the lakes in the region. Degradation as the water moves through the lake sediments was ignored. For water recharging from the deep profundal areas of the lake, we used a constant recharge temperature of 4°C, which is an average of the whole-lake temperature during fall and spring turnover. We accounted for degradation at depth using the average first-order degradation rate determined for Big Muskellunge Lake (3.8 yr<sup>-1</sup>), and durations ranging from 0.25 to 0.5 years (corresponding roughly to the average stratified periods in summer and winter). Measured concentrations were modified to reflect the values that would have occurred in the absence of degradation, and the adjusted concentrations were used to estimate apparent recharge dates in the usual manner. The resulting apparent recharge dates are given in Table 4.

[33] With a few exceptions, the apparent recharge dates in Table 4 are older than expected based on results from a calibrated groundwater flow model [Hunt et al., 2006; Pint et al., 2003; Pint, 2002]. The logical explanation for the discrepancies is degradation in the lake bed and aquifer sediments. For example, well P1-05a is a piezometer that was driven 90 cm into the lake bed. Recharge to this piezometer is undoubtedly from the littoral zone, and Darcy calculation and field temperature data suggest it is unlikely that the travel time is between 34 and 36 years. In general, the apparent recharge dates using CFC-11 are earlier than the corresponding dates for CFC-12, which is consistent with higher degradation rates for CFC-11. The only recharge date that is consistent with the model results is for well M-50, which is recharged through the unsaturated zone. Even though the atmospheric equilibration temperature was well

constrained in many of the samples ( $\pm 1^\circ\text{--}2^\circ\text{C}$ ), degradation within the lake, within the lake sediments, and during travel in the aquifer can dramatically reduce CFC concentrations, which results in apparent recharge dates that are too old (Table 4). Moreover, the amount of degradation in the sediments is expected to be heterogeneous in space and time, and as a result was not quantified and thus could not be corrected for.

#### 4.5. Implications for Recharge Dating

[34] CFC concentrations in northern temperate lakes are variable in space and time. On the basis of the observed range of temperatures at the surface of the lakes ( $2^\circ\text{--}19^\circ\text{C}$ ), the observed concentrations of CFC-12 (Figure 5) generally are near the range expected based solely on equilibrium solubility (230–530 pg/kg) using atmospheric mixing ratios corresponding to 1998 ( $537\text{ pptv} \pm 2\%$ ), the last year the lakes were exposed to the atmosphere. Thus CFC concentrations in shallow lake water can be expected to exhibit a wide seasonal range in this and similar study areas. While atmospheric equilibration temperature can be accurately estimated using dissolved gas analyses ( $\pm 1^\circ\text{--}2^\circ\text{C}$  with additional analytical cost), it is unclear if all lake-derived recharge is at equilibrium with the atmosphere. In-lake degradation takes place below the thermocline in the anoxic portions of the lakes, and additional degradation may occur as CFCs travel through the lake bed sediments and down-gradient aquifer. Dimictic lake CFC concentrations and shallow meromictic lake water concentrations are reset, or partially reset, during turnover. The completeness of the reset relative to the equilibrium with the atmosphere can vary based on the volume to surface-area ratio of the lake.

[35] Results from the four study lakes exhibit a wide range of predicted apparent recharge dates for water recharging from the lakes to the groundwater system. For the dimictic lakes, apparent recharge dates for water from the shallow zones ranged from 1988 to 1998, and the apparent recharge dates from the deep zones ranged from 1986 to 1990. The ranges of apparent recharge dates for the meromictic lake were slightly narrower and indicate older water; the apparent recharge date for water from the shallow zones ranged from 1983 to 1988, and the apparent recharge dates from the deep zones ranged from 1968 to 1973.

[36] These factors confound the use of CFCs in temperate lake systems. CFC variability with depth within the lake, degradation due to anoxic conditions, and differences in CFC concentrations after lake turnover confound simple applications of CFCs for dating lake-derived recharge in groundwater systems. The traditional approach using CFCs to date waters recharged through the unsaturated zone agreed closely with the calibrated model. Thus we conclude that uncertainty in CFC dating is primarily a concern for groundwater recharged from lakes.

## 5. Conclusions

[37] There are four main conclusions from this study.

[38] 1. There is a considerable variation in CFC concentrations and atmospheric mixing ratios in the temperate lakes sampled, both with depth and season within a given lake, and across different lakes. On the basis of results from the dimictic lakes, CFC atmospheric mixing ratios and observed degradation are likely controlled by in-lake pro-

cesses (e.g., thermal regimes and degradation rates within the anoxic regions).

[39] 2. There is significant degradation of CFC-11 in the anoxic conditions present below the thermoclines of each lake. For the meromictic lake, CFC-11 was depleted entirely at depth because it is rarely resupplied from the atmosphere by lake mixing. CFC-12 was less susceptible to degradation than CFC-11; degradation occurred only in the deep anoxic zones of the lakes.

[40] 3. CFC-12 atmospheric mixing ratios in temperate lakes may or may not be in equilibrium with atmospheric CFCs. The shallow portions of all the dimictic lakes may reach equilibrium with the atmosphere throughout the year, but the water temperature changes during this time. When lake turnover occurs, the CFC atmospheric mixing ratio in the lake water is completely reset (in the case of Big Muskellunge Lake) or partially reset (Crystal and Sparkling lakes) as the water in the lake mixes and is exposed to the atmosphere. The ratio of the volume to the surface area (mean depth) of the lake is likely an important factor in determining whether a lake reaches equilibrium with CFCs in the atmosphere during turnover. CFC-12 atmospheric mixing ratios in the meromictic lake were near equilibrium in the upper 4–6 m but were consistently undersaturated in the deeper portions of the lake.

[41] 4. The use of CFCs to date groundwater where the groundwater is recharged from lake water is more complex than the traditional method that addresses recharge through an unsaturated zone. This is a result of in-lake processes where the CFC concentration of recharge from lake waters is directly influenced by CFC degradation in the (lake) water column, CFC degradation in the lake-bed sediments, and gas exchange rates and the duration of turnover (turnover efficiency). These factors dramatically reduce CFC atmospheric mixing ratios, which results in apparent recharge dates that are too old.

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