Transit time distributions in Lake Issyk-Kul

Darryn W. Waugh,[1] Martin K. Vollmer,[2] Ray F. Weiss,[3] Thomas W. N. Haine,[1] and Timothy M. Hall[4]

Received 30 August 2002; accepted 9 October 2002; published 28 December 2002.

[1] Measurements of sulfur hexafluoride (SF_6) and chlorofluorocarbons (CFCs) are used to constrain the timescales for deep-water renewal in Lake Issyk-Kul. As these tracers have different tropospheric histories their combination provides more transport information than one tracer alone. In particular, from these measurements the mean, Γ, and standard deviation, σ, of the distributions of transit times since water made last contact with the surface can be tightly constrained. Γ is older than the age determined from SF_6 and younger than the ages from the CFCs, and increases from around 4 yrs at 200 m to around 10.5 yrs at the deepest location (655 m). σ also increases with depth and equals around 0.7 to 0.8 Γ, which corresponds to large ranges of transit times, and implies mixing processes play a major role in the transport. The approach used can also be applied to similar tracer measurements in the oceans and groundwaters to constrain transport in these geophysical systems. *INDEX TERMS:* 4808 Oceanography: Biological and Chemical: Chemical tracers; 4239 Oceanography: General: Limnology; 1832 Hydrology: Groundwater transport. **Citation:** Waugh, D. W., M. K. Vollmer, R. F. Weiss, T. W. N. Haine, and T. M. Hall, Transit time distributions in Lake Issyk-Kul, *Geophys. Res. Lett.*, *29*(24), 2231, doi:10.1029/2002GL016201, 2002.

1. Introduction

[2] Quantifying the timescales of deep-water renewal of lakes, oceans, and groundwater is important for understanding the cycling of nutrients and infiltration of pollutants. Important insight into lake transport has been obtained from measurements of time-dependent tracers, such as chlorofluorocarbons (CFCs), which enable calculation of tracer ages [e.g., *Weiss et al.*, 1991; *Peeters et al.*, 2000; *Vollmer et al.*, 2002]. However, because of mixing, these tracer ages depend on the temporal variations of the tracer, complicating their interpretation. A more fundamental description of the transport is the "transit time distribution" (or "age spectrum") [e.g., *Hall and Plumb*, 1994; *Beining and Roether*, 1996; *Varni and Carrera*, 1998]. The transit time distribution (or "TTD" for short) at an interior location of the lake is the distribution of transit times since water at that location last made contact with the surface, and depends only on the transport and not the characteristics of tracers. Given the TTD it is possible to determine the temporal variation of a tracer with known, time-varying surface concentrations. While not directly observable, information on the TTD can be inferred from measurements of tracers with different time dependencies [*Waugh et al.*, 2002]. Here we use recently reported measurements of sulfur hexafluoride (SF_6) and three chlorofluorocarbons, CFC-11 (CCl_3F), CFC-12 (CCl_2F_2), CFC-113 (CCl_2FCClF_2) in Lake Issyk-Kul, Kyrgyzstan [*Vollmer et al.*, 2002] to determine the mean, Γ, and standard deviation, σ of the TTDs in this lake.

[1]Department of Earth and Planetary Sciences, Johns Hopkins University, Baltimore, Maryland, USA.
[2]Max Planck Institute for Chemistry, Mainz, Germany.
[3]Scripps Institution of Oceanography, University of California, San Diego, La Jolla, USA.
[4]NASA Goddard Institute for Space Studies, New York, USA.

0094-8276/02/2002GL016201$05.00

2. Tracer Ages

[3] *Vollmer et al.* [2002] (hereinafter "V2002") reported measurements of SF_6, CFC-11, CFC-12, and CFC-113 from water samples taken near the center of Lake Issyk-Kul (42° 23.6′N 77°13.1′E) in September 2000. As the atmospheric concentrations of these tracers increased with time until the early 1990s and later (see Figure 1) a tracer age τ, defined as the elapsed time since the surface concentration was equal to the interior concentration, can be calculated from each of these tracers. The tracer ages for the measurements in Lake Issyk-Kul are shown as symbols in Figure 2 - see V2002 for details of the age calculations. (*Hofer et al.* [2002] also recently measured SF_6, CFC-11, and CFC-12 in Lake Issyk-Kul, and the tracer ages from their measurements agree with those in Figure 2 when the same method is used to calculate tracer ages.) All tracer ages increase with depth, but the ages differ among tracers with $\tau_{SF6} < \tau_{CFC12} < \tau_{CFC113} < \tau_{CFC11}$. These differences are due to the different atmospheric histories of the tracers, and highlight the fact that tracer ages are generally not fundamental transport timescales.

[4] Insight into the differences among the observed ages can be gained by considering tracers with quadratic temporal variations in their surface concentrations. *Waugh et al.* [2002] (hereinafter "W2002") showed that in this case the tracer age depends only on the first two moments of the TTD, i.e.,

$$\tau^2 + 2\alpha(\Gamma - \tau) - \Gamma^2 - \sigma^2 = 0, \tag{1}$$

where Γ is the mean of the TTD ("mean age"), σ the standard deviation of the TTD, $\alpha(t) = (dc_0/dt)/(d^2c_0/dt^2)$, and $c_0(t)$ is the surface concentration. (The "width", Δ, as defined in *Hall and Plumb* [1994] and W2002, equals $\sigma/\sqrt{2}$.) In the limit of linear growth, $\alpha \to \infty$, or narrow TTD, $\sigma \to 0$, (1) reduces to $\tau = \Gamma$, i.e., the tracer age equals the mean age [e.g., *Hall and Plumb*, 1994]. If $|\tau - \Gamma| \ll \Gamma$, it can be shown that

$$\tau - \Gamma \approx \frac{-\sigma^2}{2(\alpha - \Gamma)} \equiv \epsilon\sigma^2, \tag{2}$$

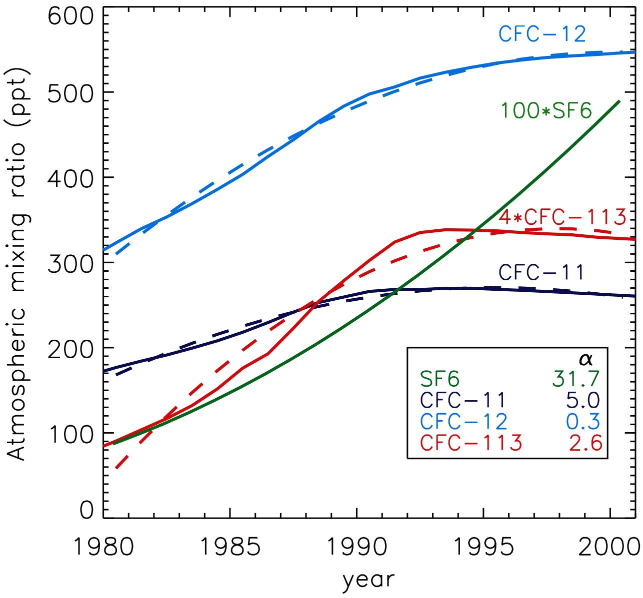

Figure 1. Time series of atmospheric concentrations, for background air in northern hemisphere troposphere, of CFCs (CFC-11, CFC-12, CFC-113) [*Walker et al.*, 2000] and SF_6 [*Maiss and Brenninkmeijer*, 1998]. The SF_6 time series is a quadratic fit to data. Dashed curves are quadratic fits to the CFC time series. The values of α (units yrs), see equation (1), in September 2000 for quadratic fits are given in the box.

i.e., the difference between the tracer and mean ages increases as σ^2. The histories of SF_6 and CFCs from 1980 to 2000 can be reasonably approximated by quadratic functions, see boundary for fits and values of α in September 2000. Assuming Γ is between 5 and 20 yrs and using these values of α, we have $\epsilon_{SF6} < 0 < \epsilon_{CFC12} < \epsilon_{CFC113} < \epsilon_{CFC11}$. This implies $\tau_{SF6} < \Gamma < \tau_{CFC12} < \tau_{CFC113} < \tau_{CFC11}$, consistent with the observed ages. The magnitude of ϵ is smallest for SF_6, with ϵ around -0.02 to -0.04 yr^{-1} for the above range of Γ.

3. Estimates of Mean Γ and Standard Deviation σ

[5] We now examine whether the differences in the ages from the measurements of the CFCs and SF_6 can be used to determine Γ and σ. Following W2002, we assume that the transport is stationary and that the TTD can be modeled as an Inverse Gaussian (IG) distribution, i.e.,

$$\mathcal{G}(t) = \sqrt{\frac{\Gamma^3}{2\pi\sigma^2 t^3}} \exp\left(\frac{-\Gamma(t-\Gamma)^2}{2\sigma^2 t}\right). \qquad (3)$$

A given tracer age τ then constrains Γ and σ to a range of values, with $\Gamma = \tau$ and $\sigma = 0$ being one limit (see W2002). The age from a second tracer will, in general, constrain Γ and σ to a different range of values, and so the combined measurements of two tracer ages will limit the possible range of Γ and σ to the intersection of the individual constraints.

[6] Figure 3 shows how the measured tracer ages at 655 m constrain Γ and σ. The contours corresponding to the lower and upper limits of the measured age for each tracer, and each measurement constrains the (Γ, σ) pair to lie between these two curves. This figure shows that the different tracer ages place different constraints on Γ and σ.

[7] The uncertainty in the observed ages is smallest for SF_6, and this tracer age places the tightest constraints on Γ and σ. Also, the slopes of the τ_{SF6} contours differ from that of the CFC ages, especially τ_{CFC11} and τ_{CFC12}, with τ_{SF6} contours moving to higher Γ for increased σ whereas the CFC age contours move to lower Γ. (These differences can again be understood by considering the quadratic fits to the temporal variations of the tracers, i.e., $\sigma^2 \approx (\tau - \Gamma)/\epsilon$ along isopleths, and $\epsilon_{SF6} < 0$ whereas $\epsilon_{CFC} > 0$.) This means that measurements of τ_{SF6} and either τ_{CFC11} or τ_{CFC12} place tight constraints on Γ and σ, i.e., there is a narrow range of (Γ, σ) space satisfying these pairs of tracer ages (intersection of green and dark or light blue curves in Figure 3). In fact, there is a very narrow range of Γ and σ where the modeled ages are within the uncertainties of the observed values for all four tracers (shaded region in Figure 3). This is also true for the measurements at other depths.

[8] At each depth the pair of Γ and σ that minimizes the weighted sum of the square of differences between the TTD and observed ages of all four tracers can be calculated. These are shown in Figure 2. Both Γ and σ increase with depth, and, consistent with the above analysis, $\tau_{SF6} < \Gamma < \tau_{CFC12}$, with τ_{SF6} closest to Γ. The ratio σ/Γ varies between 0.7 and 0.8, which corresponds to large ranges of transit times to each location, see Figure 4. Figure 2 also shows that, for all tracers, there is very good agreement between tracer ages calculated from the best-fit TTD and the observations.

[9] The determination of Γ and σ can be repeated using only a subset of the tracer ages. In particular, for any two

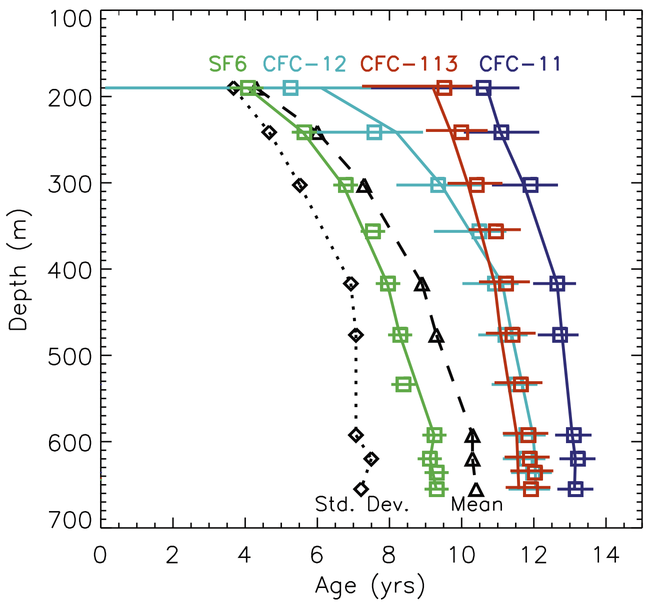

Figure 2. Vertical profiles of tracer ages, mean age, and standard deviation in Lake Issyk-Kul. The squares and horizontal lines show the observed ages plus and minus the uncertainty. The curves show the tracer ages (solid), mean age (dashed) and standard deviation (dotted) of the best-fit TTD.

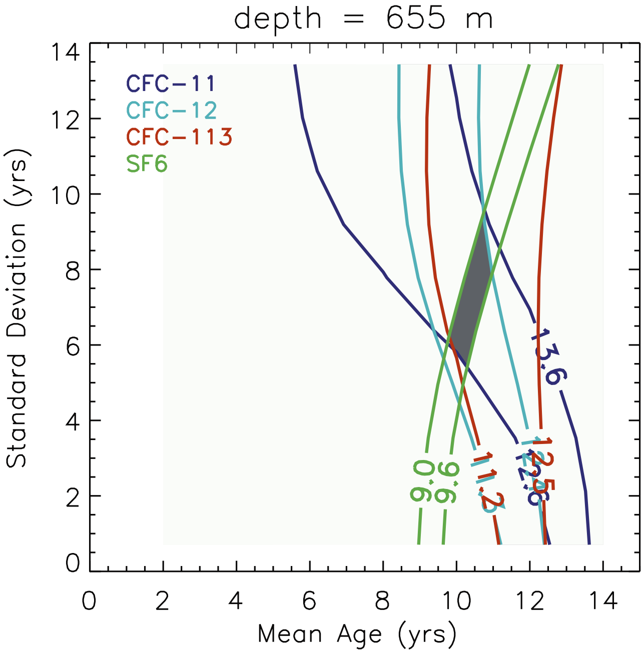

Figure 3. Variation of tracer ages with Γ and σ, for CFC-11, CFC-12, CFC-113 and SF_6 ages at 655 m. For each tracer two age isopleths are shown, one corresponding to the lower limit and the other to the upper limit of the measured age. The shaded region shows the region of (Γ, σ) space where all ages are consistent with the measurements.

tracers there is a unique (Γ, σ) pair for which the two model tracer ages exactly equal the observed ages. As discussed above SF_6 and either CFC-11 or CFC-12 are the pairs that place the tightest constrains in Γ and σ, and calculations using either pair of tracers yield very similar values of Γ and σ to those in Figure 2, with Γ varying by less than 0.2 yrs and σ by less than 0.7 yrs. Furthermore, in both cases, even though only two tracers are used to constrain the TTD all four modeled tracer ages are consistent with the observations.

[10] A further check on the estimated TTDs are the tritium-helium ages ($\tau_{3H/3He}$) [e.g., *Jenkins and Clarke*, 1976] calculated by V2002 from their tritium and noble gas measurements. The $\tau_{3H/3He}$ predicted by the above TTDs (not shown) are older than Γ and less than τ_{CFC12}, with $\tau_{3H/3He} \approx \Gamma + \frac{1}{2}\lambda\sigma^2$, where $\lambda = 0.05576\ \mathrm{yr}^{-1}$ is the decay constant of tritium, (see W2002). The agreement with the observed $\tau_{3H/3He}$ is not as good as for the CFC ages, with the modeled values on average 0.6 yrs older than observed. However, there are large uncertainties in the temporal evolution of tritium in the surface waters used in the model calculations and in the procedure used to calculate tritiogenic helium from the observations, and the model-data differences in the $\tau_{3H/3He}$ are within these uncertainties.

[11] V2002 used the measured CFC-11, CFC-12, and SF_6 concentrations to estimate the mixing and upwelling rates in a simple one-dimensional flow model, and then calculated Γ using this model. Their calculated Γ are 0.5 to 1 yr younger than our estimates. However, the tracer ages from our best-fit TTD are closer to the observed values than those from the V2002 model (τ_{SF6} from the V2002 model is younger than observed, and τ_{CFC11} and τ_{CFC12} are older), and the values of Γ from our analysis are probably more realistic.

4. Sensitivity to the Form of the Transit Time Distribution

[12] We now examine how sensitive the estimation of Γ and σ is to the assumption that the TTDs are IG distributions. We first revisit the case of tracers with quadratic temporal variation. In this case it is possible to determine Γ and σ by simultaneously solving equation (1) for two tracers, with no assumptions of the shape of the TTD. Using the quadratic fits for SF_6 and CFC-12 we obtain values of Γ and σ that are extremely close to those from the analysis using an IG distribution applied to these tracers, with Γ varying by less than 0.1 yrs and σ by less than 0.6 yrs. This excellent agreement indicates that Γ and σ estimated in the previous section are insensitive to the assumed form of the TTD.

[13] To confirm this we now consider TTDs that are a linear combination of the two IG distributions; i.e., the

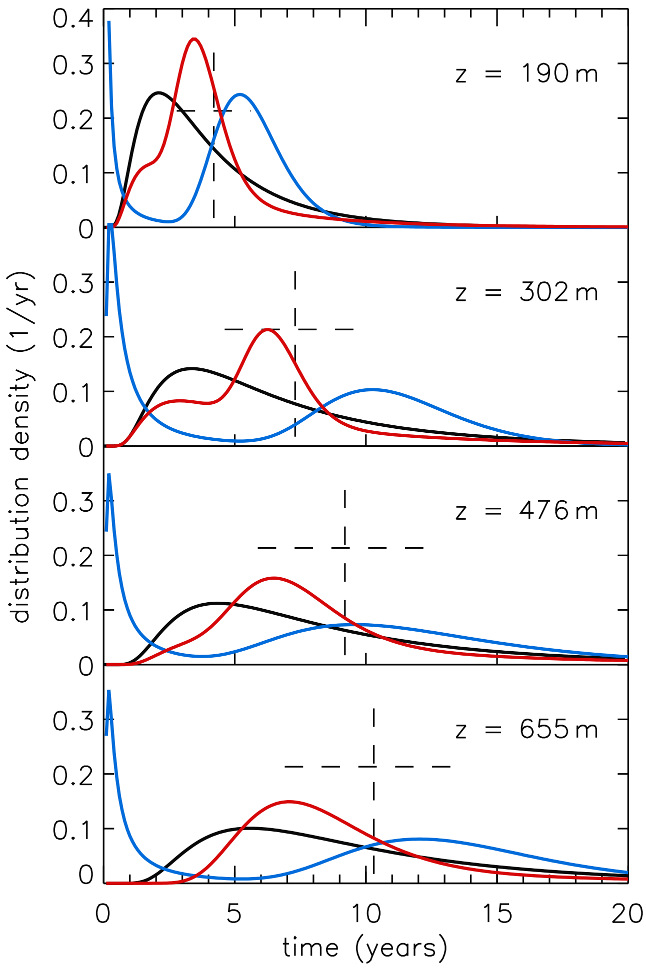

Figure 4. TTD at depths between 190 and 655 m. Dashed vertical (horizontal) lines show the mean age (standard deviation) at each depth. The black curves show IG distributions whereas the blue (red) curves show "two-IG" with lower (higher) skewness. The tracer ages from each TTD are consistent with the observed values.

TTDs are comprised of two components, each described by the distributions of the form (3). Such "two-IG" distributions have been considered in previous studies [e.g., *Andrews et al.*, 2001, W2002], and can be unimodal or bimodal (see Figure 4). As in W2002, families of two-IG TTDs with the same Γ and σ are formed and tracer ages are calculated for each member of the family. We focus here on families with the same Γ and σ as the best-fit IG TTDs at each depth. All tracer ages were found to have weak sensitivity to the form of the TTD, and for nearly all TTDs within each family the ages are within the observational uncertainty. In Figure 4 we show three TTD with best-fit values of Γ and σ for several depths. Although there are large variations in the shape of the TTDs all produce similar tracer ages (e.g., τ_{SF6} varies by less than 0.1 yrs and τ_{CFC12} varies by less than 0.5 yrs), confirming the insensitivity of estimated Γ and σ to the TTD shape.

[14] The small sensitivities of tracer ages to the TTD shape that do exist vary among the tracers. The tracer age from SF_6, whose history from 1970 to 2000 is well fit by a quadratic function, is least sensitive to the TTD shape, and the age from τ_{CFC113}, whose history over this period is most poorly fit by a quadratic, is most sensitive to the shape. The variation in tracer age with shape for fixed Γ and σ is correlated with the skewness, γ, of the TTD (the normalized third order centered moment). TTDs with low γ have young, narrow first peaks and broad second peaks older than Γ (blue curves in Figure 4 have $\gamma < 1$), and produce younger CFC ages. In contrast, TTDs with high γ have large peaks of intermediate width centered near Γ and in some cases smaller, earlier peaks (red curves in Figure 4 have $\gamma > 3.5$), and produce older CFC ages.

[15] Although the vast majority of TTDs with the best-fit Γ and σ reproduce accurately the observed tracer ages, there are, for the older values of Γ, some TTDs which produce CFC ages outside the uncertainty of the measurements. These extreme cases correspond to TTDs with very large or very small γ. However, even if the TTDs have these extreme forms the Γ and σ required to fit the tracer ages are close to the above values (e.g., Γ within 0.4 yrs).

5. Concluding Remarks

[16] The transit time distribution (TTD) is a powerful diagnostic of transport in lakes. It quantifies renewal times for deep water and can be used to determine the penetration of pollutants with known time-varying surface concentrations. The analysis here of recent measurements in Lake Issyk-Kul has shown that, because their atmospheric histories differ, SF_6 and CFC-12 or CFC-11 in "young" waters (transit times less than 30 years) tightly constrain the mean, Γ, and the standard deviation, σ of the TTD. Diagnosing transport in this way will also be of use in oceans and groundwaters. Simultaneous measurements of these tracers have recently been made in the ocean [e.g., *Law and Watson*, 2001; *Vollmer and Weiss*, 2002], and application of our method to these and other measurements may provide estimates of TTDs for oceans and groundwaters.

[17] Although the measurements of SF_6 and CFCs tightly constrain Γ and σ they do not constrain higher order moments. The TTDs shown above vary smoothly with time, but TTDs with additional small amplitude high frequency variability would also fit the observed tracers. Furthermore, as shown in Figure 4, TTDs with very different shapes can have the same Γ and σ. These different shapes can represent different transport scenarios. For example, the TTD for one-dimensional advection with along-flow diffusion is the IG distribution (3), and the IG TTD shown in Figure 4 are consistent with such a one-dimensional flow. On the other hand, the bimodal TTDs in Figure 4 with two very distinct peaks correspond to flows with two primary sources or pathways, with the young, narrow peak corresponding to rapid ventilation, perhaps due to convective events. Incorporation of other aspects of the flow, from measurements or models, into the analysis of tracer data may provide some insight into which transport scenario, and TTDs, are more realistic.

[18] **Acknowledgments.** We thank Peter Schlosser for the tritium and noble gas measurements.

References

Andrews, A. E., K. A. Boering, S. C. Wofsy, B. C. Daube, D. B. Jones, S. Alex, M. Loewenstein, J. R. Podolske, and S. E. Strahan, Empirical age spectra for the midlatitude lower stratosphere from in situ observations of CO_2: Quantitative evidence for a subtropical "barrier" to horizontal transport, *J. Geophys. Res.*, *106*, 32,295–32,314, 2001.

Beining, P., and W. Roether, Temporal evolution of CFC 11 and CFC 12 concentrations in the ocean interior, *J. Geophys. Res.*, *101*, 16,455–16,464, 1996.

Hall, T. M., and R. A. Plumb, Age as a diagnostic of stratospheric transport, *J. Geophys. Res.*, *99*, 1059–1070, 1994.

Hofer, M., F. Peeters, W. Aeschbach-Hertig, M. Brennwald, Holocher, D. M. Livingstone, V. Romanovski, and R. Kipfer, Rapid deep-water renewal in Lake Issyk-Kul (Kyrgystan) indicated by transient tracers, *Limnol. Oceanogr.*, *47*, 1210–1216, 2002.

Jenkins, W. J., and W. B. Clarke, The distribution of ^{3}He in the Western Atlantic Ocean, *Deep-Sea Res.*, *23*, 481–494, 1976.

Law, C. S., and A. J. Watson, Determination of Persian Gulf Water transport and oxygen utilization using SF_6 as a novel transient tracer, *Geophys. Res. Lett*, *28*, 815–818, 2001.

Maiss, M., and C. A. M. Brenninkmeijer, Atmospheric SF_6: Trends, sources, and prospects, *Environ. Sci. Technol.*, *32*, 3077–3086, 1998.

Peeters, F., R. Kipfer, M. Hofer, D. M. Imboden, and V. M. Domysheva, Vertical turbulent diffusion and upwelling in Lake Baikal estimated by inverse modeling of transient tracers, *J. Geophys. Res.*, *105*, 3451–3464, 2000.

Varni, M., and J. Carrera, Simulation of groundwater age distributions, *Water Resour. Res.*, *34*, 3271–3281, 1998.

Vollmer, M. K., and R. F. Weiss, Simultaneous determination of sulfur hexafluoride and three chlorofluorocarbons in water and air, *Mar. Chem.*, *78*, 137–148, 2002.

Vollmer, M. K., R. F. Weiss, P. Schlosser, and R. T. Williams, Deep water renewal in Lake Issyk-Kul, *Geophys. Res. Lett.*, *29*, 10.1029/2002GL014763, 2002.

Walker, S. J., R. F. Weiss, and P. K. Salameh, Reconstructed histories of the annual mean atmospheric mole fractions for the halocarbons CFC-11, CFC-12, CFC-113, and carbon tetrachloride, *J. Geophys. Res.*, *105*, 14,285–14,296, 2000.

Waugh, D. W., T. M. Hall, and T. W. N. Haine, Relationships among tracer ages, *J. Geophys. Res.*, in press, 2002.

Weiss, R. F., E. C. Carmack, and V. M. Koropalov, Deep-water renewal and biological production in Lake Baikal, *Nature*, *349*, 665–669, 1991.

D. W. Waugh and T. W. N. Haine, Department of Earth and Planetary Sciences, Johns Hopkins University, Baltimore, MD 21218, USA. (waugh@jhu.edu; thomas.haine@jhu.edu)

M. K. Vollmer, Max Planck Institute for Chemistry, P.O. Box 3060, D-55020 Mainz, Germany. (vollmer@mpch-mainz.mpg.de)

R. F. Weiss, Scripps Institution of Oceanography, University of California, San Diego, La Jolla USA. (rfweiss@uscd.edu)

T. M. Hall, NASA Goddard Institute for Space Studies, 2880 Broadway, New York, NY 10025, USA. (thall@giss.nasa.gov)