Chapter 4

Lake Malawi/Nyasa Deep Water Renewal

M. K. Vollmer and R. F. Weiss
Scripps Institution of Oceanography, University of California at San Diego, La Jolla, California, USA 92093-0220

H. A. Bootsma
SADC/GEF Lake Malawi/Nyasa Biodiversity Conservation Project, P.O. Box 311, Salima, Malawi

Introduction

Lake Malawi/Nyasa, located in the East African Rift, is meromictic owing to a permanent but periodically weak stratification maintained by small gradients in temperature, salts, and dissolved uncharged species (Wüest et al. 1996). As a consequence of this meromixis and the lake's internal biological cycle, the surface water is depleted in nutrients and biogenic material accumulates in the anoxic deep water. In order to study the cycling of these nutrients, the distribution of pollutants, and the lake's responses to external long-term perturbations, it is essential to know the deep-water renewal rates. In 1976, Gonfiantini et al. (1979) conducted a mixing study on Lake Malawi/Nyasa using tritium produced by the atmospheric testing of thermonuclear weapons as a tracer. Using a 3-box model, they calculated a surprisingly fast 5-year average exchange time of the anoxic hypolimnion with respect to the metalimnion. The renewal time of the metalimnion with respect to the epilimnion was calculated to be 4 years.

The purpose of the current study is to give an independent estimate of a deep-water renewal rate using measurements of the gaseous transient tracer CCl_2F_2 (chlorofluorocarbon-12 or CFC-12). Anthropogenically produced CFC-12 has been increasing in the atmosphere since its production began in the 1930s. This gas dissolves into the lake's surface water from the atmosphere, labeling the water with a time-dependent concentration signal as it is mixed into the interior of the lake. Measurements of chlorofluorocarbons (CFCs) in the water column can therefore help to identify the origin of a water parcel and its age, defined as the time elapsed since it left the surface. CFCs have been used extensively in oceanographic studies (e.g. Gammon et al. 1982; Weiss et al. 1985; Pickart et al. 1989; Doney and Bullister 1992) to help understand the circulation and dynamics of the oceans. The successful application of CFC-12 as a limnological tracer in a mixing study for Lake Baikal (Weiss et al. 1991) has led to the application of this technique to Lake Malawi/Nyasa.

Methods

A hydrographic and geochemical survey was conducted on Lake Malawi/Nyasa in September 1997 aboard R/V *Usipa*. CTD (conductivity-temperature-depth) data were collected by a Seabird SBE-19 profiler, fitted with an O_2 electrode, at 27 routinely-visited stations along a north-south transect. At selected stations water samples were taken, using 5 liter Hydro-Bios bottles, for the analysis of nitrogen, phosphate, carbon species, the isotopes $\delta^{13}C$ and $\Delta^{14}C$, the transient tracers CFCs, and helium-3 and tritium, and the gases N_2O and N_2/Ar. In addition to the routinely visited stations, additional sampling for all the above-mentioned parameters was performed at the location with the lake's maximum depth of about 700 m (Station 940; 11°8.6' S, 34°19.2' E), northeast of Nkhata Bay.

With the exception of helium-3 and tritium, all the measurements have been completed. We report here the first interpretations of the CFC results at deep Station 940 – further measurement results and interpretations will be published elsewhere.

Samples for CFCs were collected at 3 stations, taking special precautions to avoid contamination from the sampling bottles and from ambient air (Bullister and Weiss 1988). These samples were sealed into glass ampoules, specifically following the technique developed at the University of Bremen (Klatt 1997; Bulsiewicz et al, 1998), and were transported to the Scripps Institution of Oceanography for analysis.

The CFCs were analyzed by electron capture detection gas chromatography in a modified purge-and-trap system originally designed by Bullister and Weiss (1988). The instrument was adapted for the ampoule technique, and the NaOH-impregnated absorbent Ascarite was used to remove any traces of H_2S (Bullister and Lee 1995). Our first attempt to measure Lake Malawi/Nyasa samples was hindered by the presence of volatile hydrocarbons at elevated concentrations which interfered with the quantification of the CFC peaks. Therefore the chromatographic method was altered and a better separation of CFC-12 from hydrocarbons was achieved using Porapak Q and Molecular Sieve 5A columns. This revised chromatographic method did not allow for the measurement of CCl_3F (CFC-11) or CCl_2FCClF_2 (CFC-113), a compromise which was acceptable because these compounds are degraded in anoxic waters (Bullister and Lee 1995; Tanhua 1997). Instead, the analytical method was optimized to measure CFC-12 and N_2O. The analytical precisions (1σ) of the CFC-12 standard gas and water sample analyses, as determined from replicate samples, were 0.5% and 1.4% respectively. Results are reported on the SIO-1993 calibration scale (Cunnold et al. 1994).

Results

The results for potential temperature and CFC-12 concentration profiles at Station 940 are listed in Table 4.1, and are plotted together with the dissolved oxygen profile in Fig. 4.1. The CFC-12 profile shows a concentration decrease from the surface to the maximum depth, with distinct inflections at the depths of 105 and 220 m which can also be found in profiles for other parameters, such as in the oxygen concentration profile. These transitions may be used to distinguish three different layers in the lake following a terminology suggested previously (Gonfiantini et al. 1979). We therefore designate the 105 m thick surface layer as the epilimnion, the middle layer as the metalimnion and the deep water below the oxic/anoxic boundary as the hypolimnion, although these definitions do not match their more traditional meaning used to describe holomictic lakes.

In the epilimnion the CFC-12 concentrations are rather uniform at about 1.4 pmol/kg (10^{-12} mol/kg), an indication that the preceding winter mixing reached to a depth of 105 m. At a depth of 10 m, CFC-12 is oversaturated by about 1% with respect to a mean 1997 Southern Hemisphere atmospheric CFC-12 background concentration (Walker et al, 1998) of 528 ppt (dry air mole fraction in parts-per-trillion, or parts in 10^{12}), and a mean atmospheric pressure (measured at Senga Bay) of 961 mbar (H. Bootsma, unpublished data). The solubility for CFC-12 (Warner and Weiss 1985) was calculated for a water temperature of 25.1 ºC and a salinity of 0.209 g/kg, based on the ionic fraction of dissolved compounds as determined from the in-situ conductivity (Wüest et al. 1996). In the metalimnion, the CFC-12 concentrations decrease to about 1 pmol/kg at the oxic/anoxic boundary, below which the CFC-12 concentrations decrease steeply to about 0.4 pmol/kg in the lower part of the hypolimnion. The potential temperature in the lake decreases gradually throughout the epilimnion and the metalimnion and reaches nearly isothermal conditions at about 22.7 °C in the hypolimnion. The temperature has an overall stabilizing effect on the water column, although during the wintertime, when epilimnetic temperatures fall to around 23.5 °C (Patterson and Kachinjika 1995), this effect can be very weak. To maintain this temperature gradient in the lake, sporadic intrusions of cold water from the surface directly into the hypolimnion must occur, thus compensating for heat diffusion from above and the geothermal warming from below (Halfman 1993). Such intrusions must result in an overall upwelling in the deep water, a hypothesis supported by the convex upward curvature of the vertical

Table 4.1. Lake Malawi/Nyasa potential temperature and CFC-12 profiles at Station 940, [11°8.6' S, 34°19.2' E], September 13, 1997. Potential temperature is calculated from *in situ* CTD temperature according to Wüest et al. (1996), which includes the freshwater-specific thermal expansivity and the specific heat at constant pressure (Chen and Millero 1986). The potential temperature of the deepest CTD measurement at 681 m is listed for the deepest water sample at 683 m.

Depth [m]	Potential Temperature [°C]	CFC-12 [pmol/kg]
10	25.12	1.426
50	24.24	1.409
105	23.54	1.375
120	23.34	1.271
140	23.15	1.202
170	23.03	1.150
190	22.98	1.072
200	22.95	1.021
215	22.94	0.998
230	22.88	0.914
245	22.84	0.828
300	22.76	0.578
360	22.72	0.476
420	22.70	0.429
480	22.69	0.405
530	22.68	0.391
570	22.68	0.388
610	22.68	0.380
640	22.67	0.376
670	22.67	0.365
683	22.67	0.363

profiles of conservative properties, such as potential temperature, at depths below the influence of the seasonality of the upper water column.

We have calculated the CFC-12 *apparent* age for the water column at Station 940. This *apparent* age is defined for a water sample as the sampling date minus the date at which the epilimnion had the same CFC-12 concentration (Fig. 4.2) as is measured in the sample. The apparent age may differ from the *true* age of a water sample when there is subsurface mixing. Here the *true* age is defined as the volume-weighted average of the individual ages of the components that comprise the mixture. In the special case where the CFC-12 atmospheric source function has been effectively linear over the range of ages of a mixture's components, the apparent age approximates the true age (Weiss et al. 1991). Otherwise, mixing components from an age range during which the CFC-12 atmospheric increase was accelerating with time (i.e. before the 1970s) will lead to an apparent age for the mixture which is less than the true age, while mixtures from an age range during which the atmospheric increase was decelerating with time (i.e. after the mid-1980s) will lead to an apparent age which is greater than the true age. The CFC-12 apparent age profile for Station 940 is plotted in Fig. 4.3 for depths below the

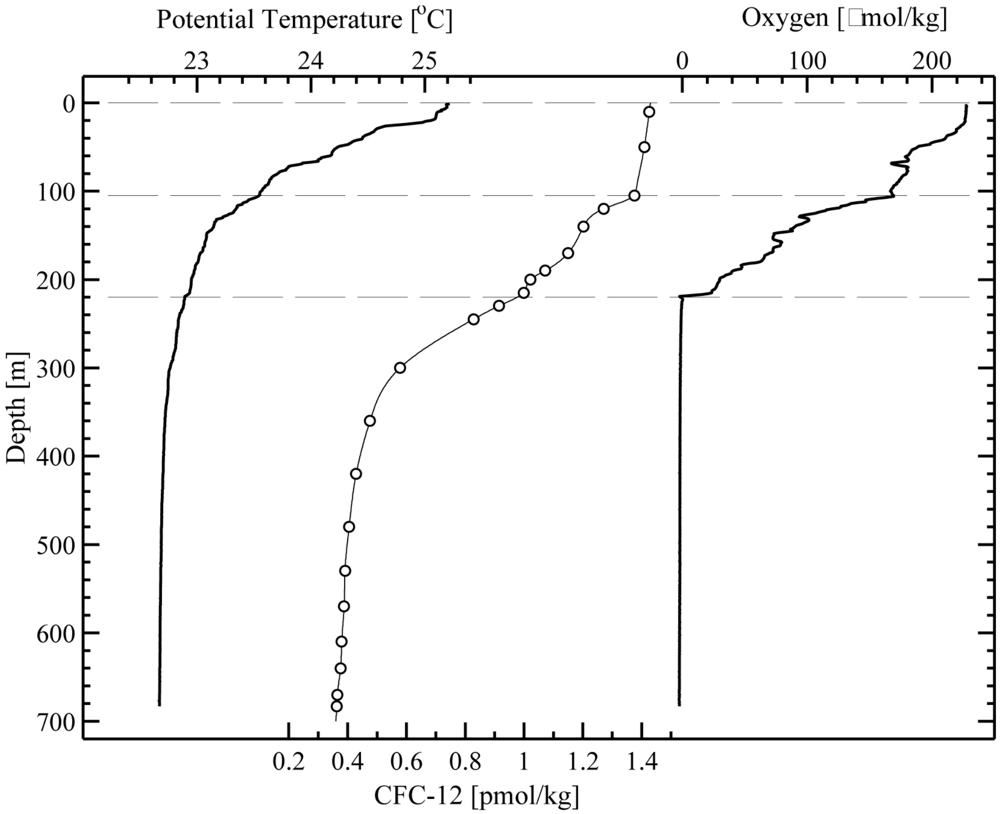

Fig. 4.1. Profiles for potential temperature, CFC-12 and oxygen concentration at the deep Station 940, September 13, 1997. Dashed lines denote the lake's surface, and the boundaries between epilimnion and metalimnion at 105 m and between metalimnion and hypolimnion at 220 m.

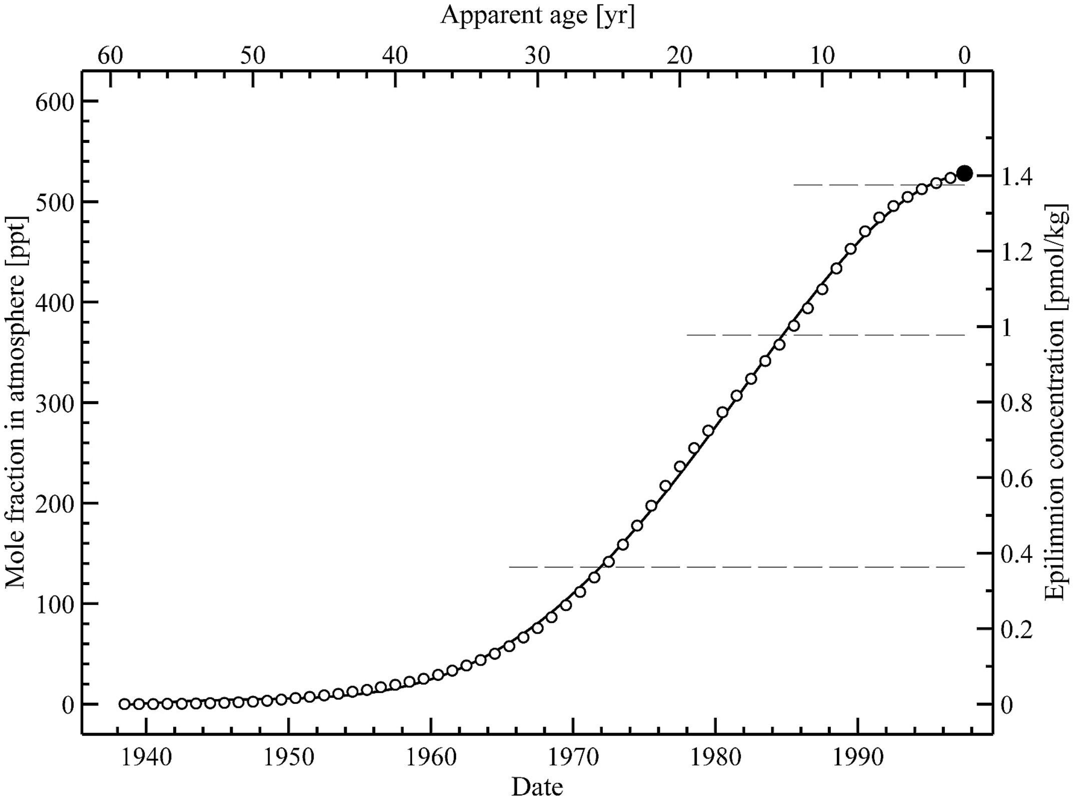

Fig. 4.2. Atmospheric background concentrations vs. time (o) for CFC-12 in the Southern Hemisphere (Walker et al. 1998), fitted by least squares to a sixth-order polynomial function (solid line). The unit is dry air mole fraction expressed as parts in 10^{12} (ppt), labeled on the left axis. The right axis gives CFC-12 concentrations in the epilimnion vs. time, obtained by normalizing the atmospheric trend to a mean epilimnetic concentration of 1.41 pmol/kg for September 1997 (•). Dashed lines show the minimum CFC-12 concentration observed and the concentrations at the boundaries between the layers.

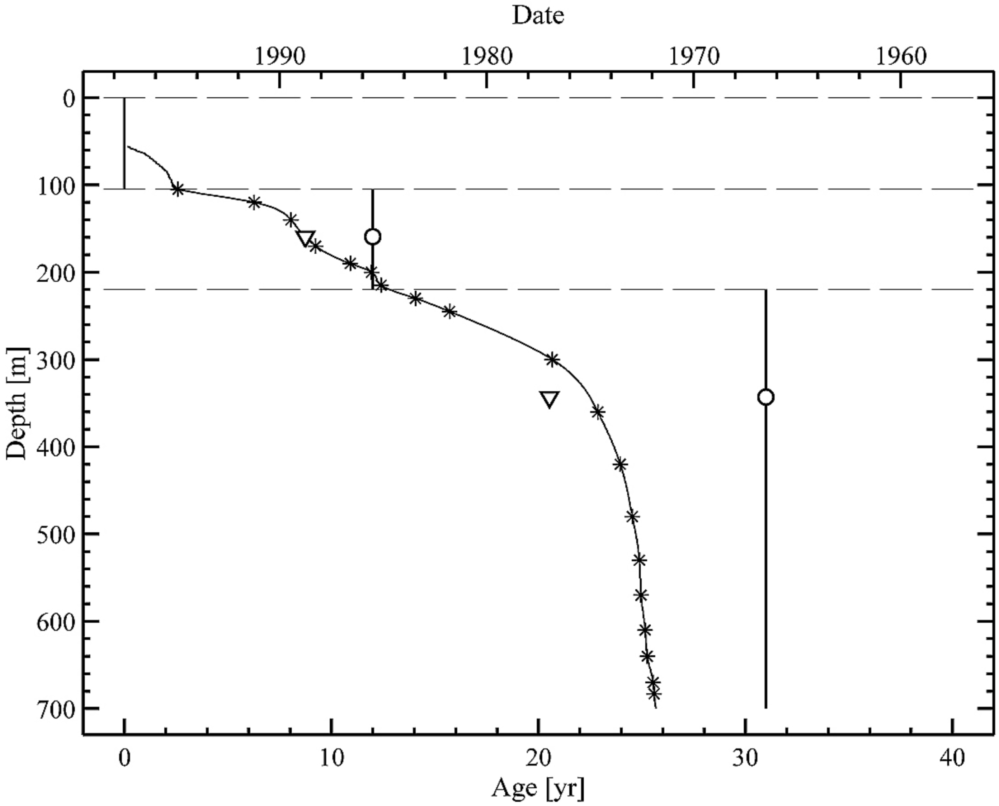

Fig. 4.3. Age distribution for Lake Malawi/Nyasa water based on the CFC-12 profile at Station 940. The CFC-12 apparent ages of the water (*) and the box model ages for the three layers (vertical solid lines) are shown vs. depth. The volumetrically averaged apparent ages (▽) and the box model ages (○) for the hypolimnion and metalimnion are shown at the volumetric mid point of each layer. Dashed lines denote the lake's surface and the boundaries between epilimnion and metalimnion at 105 m and between hypolimnion at 220 m.

upper epilimnion. No apparent ages are plotted for the upper epilimnion where the measured CFC-12 concentrations exceed the volumetrically-averaged epilimnetic CFC-12 concentration. Using the hypsographic curve based on the Lake Malawi bathymetric map of T. Johnson and B. Halfman (Large Lakes Observatory, University of Minnesota, Duluth), we calculate the volumetrically-averaged CFC-12 apparent ages of the metalimnion and hypolimnion as 8.7 years and 20.5 years, respectively (Fig. 4.3).

To calculate the exchange rates between the layers we use a 3-box model, which follows the approach of Gonfiantini et al. (1979). In order to make our results directly comparable to theirs, we first divide the lake into equal-volume layers, separated at depths of 100 m and 250 m. The resulting volumetrically averaged CFC-12 concentrations in the metalimnion and hypolimnion are calculated as 1.13 and 0.53 pmol/kg respectively. The exchanges of water between the epilimnion and metalimnion, and between the metalimnion and hypolimnion, are modeled using two coupled first-order differential equations:

$$\frac{dc_2}{dt} = k_2 c_1 - \left(k_2 + k_3 \frac{V_3}{V_2}\right) c_2 + k_3 \frac{V_3}{V_2} c_3 \tag{1}$$

and,

$$\frac{dc_2}{dt} = k_2 c_1 - \left(k_2 + k_3 \frac{V_3}{V_2}\right) c_2 + k_3 \frac{V_3}{V_2} c_3 \tag{2}$$

where *c* and *V* denote the concentrations and volumes of each of the three *i* boxes respectively. The *V*s cancel under the assumption of equal box volumes, but they are included in the equations for use in later calculations, where specific box volumes are used. The source function c_1, the epilimnetic CFC-12 concentration, is calculated by normalizing the mean epilimnetic concentration of 1.41 pmol/kg to the atmospheric source function, which is equivalent to assuming that the epilimnetic water at a wintertime temperature of about 23.5 ºC (Patterson and Kachinjika 1995) is about 94% saturated. The constants k_2 and k_3 are the exchange coefficients between the epilimnion and the metalimnion, and between the metalimnion and the hypolimnion, respectively. The water exchange fluxes between the epilimnion and the metalimnion, ϕ_2, and between the metalimnion and the hypolimnion, ϕ_3, are given by $\phi_2 = k_2 \times V_2$ and $\phi_3 = k_3 \times V_3$. Analytical solutions can be found for c_2 and c_3, and numerical solutions yield exchange times between the layers of $1/k_2 = 7$ yr and $1/k_3 = 22$ yr, which are significantly longer than the 1976 tritium-based results of Gonfiantini et al. (1979).

The model calculations have also been performed for layers divided at 105 m and 220 m, which better match the inflections in our measured profiles. The resulting volumes and volumetrically averaged CFC-12 concentrations are 2.33×10^{12} m^3 and 1.16 pmol/kg for the metalimnion, and 2.72×10^{12} m^3 and 0.59 pmol/kg for the hypolimnion. These values yield similar exchange times of $1/k_2 = 5.5$ yr and $1/k_3 = 19$ yr, again longer than the earlier tritium-based study.

The mean box model ages of the water in the two subsurface boxes, τ_2 and τ_3, are related to the exchange times by the following relationships derived from Equations 1 and 2:

$$\frac{dc_2}{dt} = k_2 c_1 - \left(k_2 + k_3 \frac{V_3}{V_2}\right) c_2 + k_3 \frac{V_3}{V_2} c_3 \tag{3}$$

and,

$$\frac{dc_2}{dt} = k_2 c_1 - \left(k_2 + k_3 \frac{V_3}{V_2}\right) c_2 + k_3 \frac{V_3}{V_2} c_3 \tag{4}$$

For the model solution with the upper boundaries of the metalimnion and the hypolimnion at 105 m and 220 m, respectively, τ_2 = 12 yr and τ_3 = 31 yr (Fig. 4.3). For comparison, the 1976 tritium based model solutions of Gonfiantini et al. (1979) give values of τ_2 = 8 yr and τ_3 = 13 yr.

The CFC-12 based box model ages are higher than the mean apparent ages in both the metalimnion and the hypolimnion. It is most likely that these apparent ages underestimate the true ages, since older (pre-1970s) individual water parcels undoubtedly contribute to the water column mixtures below the epilimnion. However it is impossible to quantify the true ages of these mixtures without a model which accurately represents the mixing history of the water column.

Conclusions

Our 3-box model for CFC-12 in 1997 yields an exchange time between the hypolimnion and the metalimnion which is more than 3 times longer than that estimated by Gonfiantini et al. (1979) based on the tritium distribution measured in 1976. The reasons for this difference may be related to the incomplete representation of the actual mixing processes in this box model, combined with the different temporal histories of the source functions for tritium and CFC-12. These mixing rates must be treated with caution, since this 3-box model clearly oversimplifies the actual ventilation processes occurring in Lake Malawi/Nyasa. In fact, as noted earlier, this model is physically unrealistic because it does not allow for the direct intrusion of cold water from the surface into the hypolimnion which is required to maintain the temperature gradient. On the other hand, a model which would include such processes cannot be solved without additional observational constraints. It is hoped that the results of the analyses of our helium-3 and tritium samples, collected simultaneously with our CFC-12 samples, as well as the incorporation of temperature into an improved model representation, will lead to a more realistic characterization of deep water ventilation rates. Another underlying assumption in our box model calculations is that mixing and ventilation processes have been at steady-state for the time period representing the true mixing and ventilation processes within the lake. However, the structure of the water column may have changed over the last decades due to climatic variability and the associated responses of an occasionally weakly-stratified lake to external perturbations. In this case, mixing conditions may have altered, leading to changes in deep water renewal rates over time. With the present tracer study we also have not attempted to identify and quantify specific mixing processes, but rather to give an average renewal rate for the deep water. Better characterization and quantification of mixing processes in the lake are necessary in order to improve our understanding of deep water renewal.

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