# Exceptional mixing events in meromictic Lake Lugano (Switzerland/Italy), studied using environmental tracers

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## Abstract

The deep northern basin of Lake Lugano was permanently stratified over the last 4 decades because of mineralization in response to strong eutrophication. However, two consecutive cold and windy winters (2004 2005 and 2005 2006) destabilized the water column and led to two exceptionally strong mixing events. The conductivity, temperature, and depth time series data from 1995 to 2006 allowed the reconstruction of the evolution of the water body that made deep convective mixing possible. Over the years 1995 2006, the stability of the water column decreased continuously in winter, reaching a neutral stability at the end of the study period. The Schmidt stability values observed in the winters of 2004 2005 and 2005 2006 were virtually zero. Analyses of helium isotopes, tritium, sulfur hexafluoride, and chlorofluorocarbons in water samples collected immediately after the two mixing events revealed large changes in the tracer concentration profiles and permitted comparisons of the apparent water ages in Lake Lugano with previous measurements. Tracer concentration profiles became more homogeneous and approached atmospheric equilibrium concentrations in the time series. The tracer data, along with changes observed in the physical parameters of the water column, demonstrate the considerable deep water renewal and gas exchange with the atmosphere that has taken place.

Lake Lugano is located on the border between Switzerland and Italy (46°00′N, 9°00′E, 271 m above sea level, *see* Fig. 1). An artificial dam that was built on a moraine front in the first half of the 20th century separates the lake into two basins. This study focuses only on the deep northern basin ($z_{max}$ = 288 m), which can be treated as an individual lake with the connection to the southern basin acting as an outflow. The limited water throughflow with respect to the volume of the northern basin results in a relatively high hydrological residence time of ~12.3 yr (Barbieri and Polli 1992).

During approximately 40 yr, the northern basin of Lake Lugano was meromictic and the water column was stagnant and anoxic below ~100-m depth (Barbieri and Mosello 1992; Aeschbach-Hertig et al. 2007). Strong eutrophication during the second half of the 20th century caused chemical stratification of the water column (Wüest et al. 1992) and the formation of a permanent *monimolimnion* (Findenegg 1935). The causes and the evolution of meromictic conditions have also been studied in various other lakes (Jellison et al. 1998; Stevens and Lawrence 1998; Boehrer and Schultze 2008). However, it has to be noted that despite the dominant stratification in these meromictic lakes, turbulent vertical mixing occurs in the entire water column and hypolimnion and monimolimnion are not completely separated with respect to the transport of dissolved substances.

Environmental measures to reduce external phosphorus loading of the northern basin of Lake Lugano that were implemented in 1976 helped to bring about a significant improvement in the water quality of the uppermost 100 m (Barbieri and Mosello 1992; Barbieri and Simona 2001). In the monimolimnion, however, phosphorus concentrations remained high and anoxic conditions continued to prevail. In winter 1998 1999, the first subtle signs of decreasing stability in the water column were observed. During the cold and windy winter of 2004 2005 (CIPAIS 2005), convective mixing reached the bottom of the lake for the first time in decades. This exceptional mixing event erased the chemical stratification of the northern basin of Lake Lugano and facilitated even stronger deep-water renewal during the following winter of 2005 2006, which was unusually cold (CIPAIS 2006). In contrast, during the mild winter of 2006 2007 vertical mixing in the lake reached a maximum depth of only 80 m (Ufficio Protezione e Depurazione Acque pers. comm.). Weak water exchange due to mild winters has also been reported in other Swiss lakes (Livingstone 1997). Given the present warming trend in the climate, weak deep-water renewal due to high winter temperatures might become more frequent, potentially threatening lake water quality.

This study investigates the causes and effects of the recent exceptional mixing events in Lake Lugano. We use data on temperature, electrical conductivity, and oxygen, which are recorded every 2 weeks as a part of the regular water-quality monitoring of the lake, to illustrate the processes that led to the "lake overturn" in 2005 and 2006. The progressive vertical mixing is clearly manifested in the concentration changes of dissolved noble gases, $SF_6$, and chlorofluorocarbons (CFCs), which were measured over a time period of 5 yr.

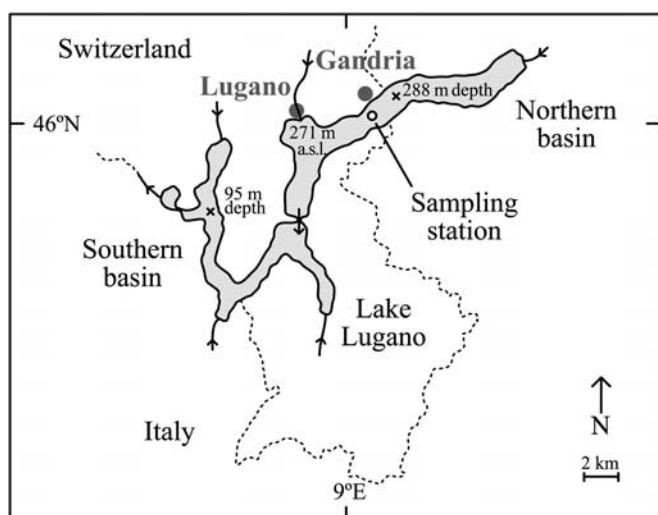* Corresponding author: rolf.kipfer@eawag.ch

Fig. 1. Map of Lake Lugano. The sampling station is located in the deepest part of the lake in the northern basin.

Aeschbach-Hertig et al. (2007) presented an extensive environmental tracer study of Lake Lugano on the basis of helium (He), tritium ($^3H$), and $SF_6$ data that documented the weak vertical mixing that occurred in the northern basin during 1990 2001. CFC data from 2001 and 2006 could not be used to analyze the dynamics of the water column because of CFC-12 contamination and CFC-11 degradation. No significant trend in the rate of deep-water renewal was found. New tracer data from May 2005 and April 2006, however, differ substantially from earlier data, indicating that considerable deep-water renewal and gas exchange has occurred recently.

## Methods

*Sampling* In this study, all conductivity, temperature, and depth (CTD) profiles and water samples were taken at a station in the deepest part of Lake Lugano near the village of Gandria (Fig. 1). Profiles of temperature ($T$), electrical conductivity ($\kappa_{20}$, i.e., normalized to a water temperature of 20°C using a conversion by Bührer and Ambühl [1975]), and oxygen ($O_2$) are measured every 2 weeks by the Ufficio Protezione e Depurazione Acque (UPDA) formerly Laboratorio Study Ambientali (LSA) and published in periodical reports (LSA 1981 2000; UPDA 2006). The CTD data used for this study cover the years 1995 2006, including unpublished measurements for 2006. CTD profiles were acquired using an Idronaut Ocean Seven 316 multiparameter probe (accuracy of ±0.003°C for $T$, ±3 $\mu S$ cm$^{-1}$ for $\kappa_{20}$, and ±0.1 mg L$^{-1}$ for $O_2$; resolution of 0.0007°C for $T$, 1 $\mu S$ cm$^{-1}$ for $\kappa_{20}$, and 0.01 mg L$^{-1}$ for $O_2$).

Water samples for transient tracer analysis were taken using Niskin bottles. Any contact of the water samples with air during sampling was carefully avoided. The water samples for He and $^3H$ analyses were transfered to copper tubes on the ship, and the tubes were sealed gas tight using pinch-off clamps. Samples for the analysis of $SF_6$ and CFC-12 were stored in stainless steel cylinders equipped with two plug valves. The transient tracer profiles sampled on 03 May 2001, 24 May 2005, and 25 April 2006 are discussed in this study (Table 1).

*Transient tracers* Helium concentrations and isotope ratios were measured using noble gas mass spectrometry in the Noble Gas Laboratory at ETH Zürich (Beyerle et al. 2000). Tritium concentrations were determined by the $^3He$ ingrowth method (Clarke et al. 1976), using a high-sensitivity compressor-source noble gas mass spectrometer (H. Baur unpubl.). Typical measurement precision is ±0.5% for He concentrations, ±1.3% for $^3He$:$^4He$ ratios, and ±5.1% for $^3H$. The determination of concentrations of $^3H$ and $^3He$ in the same water sample allow the apparent $^3H$-$^3He$ water age to be calculated (Torgersen et al. 1977). For this calculation, the measured total $^3He$ concentration needs to be separated into the tritiogenic $^3He_{tri}$ ($^3He$ produced by the decay of $^3H$), atmospheric, and terrigenic components (Kipfer et al. 2002). Atmospheric equilibrium concentrations of He in the water column were calculated from the solubilities of Weiss (1971), as recommended by Kipfer et al. (2002), using the water temperature and salinity prevailing at the respective sampling depth and the mean atmospheric pressure observed in Lugano (983.9 hPa; Aeschbach-Hertig et al. 2007). Salinity ($S$) was calculated from the measured conductivity using a linear conversion of $\kappa_{20}$ into $S$ (1 $\mu S$ cm$^{-1}$ = 0.89 × 10$^{-3}$ g kg$^{-1}$; Wüest et al. 1992).

$SF_6$ and CFC-12 were analyzed simultaneously on a gas chromatograph equipped with an electron capture detector after extraction and purification in a vacuum line. Measurement precision for this method is ±5%, as determined from the reproducibility of replicate samples with modern concentrations. Detection limits are 0.07 fmol kg$^{-1}$ for $SF_6$ and 2 fmol kg$^{-1}$ for CFC-12. The temporal evolution of the atmospheric $SF_6$ and CFC-12 concentrations is imprinted in surface waters by gas exchange. As $SF_6$ and CFC-12 concentrations in lakes are not significantly affected by degradation processes or sources other than the atmosphere, the prevailing concentrations can be interpreted in terms of the time elapsed since a given water element was last in contact with the atmosphere. This time is called the water age (Hofer et al. 2002). To determine the apparent $SF_6$ and CFC-12 water ages, the atmospheric mixing ratios that correspond to solubility equilibrium with the observed water column concentrations were calculated and compared with the temporal evolution of the atmospheric concentrations. Atmospheric equilibrium concentrations in Lake Lugano were determined using the atmospheric histories of Maiss and Brenninkmeijer (1998) for $SF_6$ and of Walker et al. (2000) for CFC-12, and the solubility data of Bullister et al. (2002) for $SF_6$ and of Warner and Weiss (1985) for CFC-12.

## Results

*Temperature, conductivity, and dissolved oxygen* The temporal evolution of temperature ($T$), electrical conductivity ($\kappa_{20}$), and oxygen concentration ($O_2$) in the water column from 1995 to 2006 is shown in Fig. 2. As already documented in our earlier work (Aeschbach-Hertig et al. 2007), the deep-water temperature of Lake Lugano gradu-

Table 1. Concentrations of ³H, He isotopes, SF₆, CFC 12, apparent SF₆ ages, and ³H ³He ages in Lake Lugano. Data of 2001 from Aeschbach Hertig et al. (2007).

| Depth (m) | $^3H$ (TU) | $^4He$ $(10^{-8}$ cm³ STP* g$^{-1})$ | $^3He : ^4He$ $(10^{-6})$ | $SF_6$ (fmol kg$^{-1}$) | CFC 12 (pmol kg$^{-1}$) | $^3H$ $^3He$ age (yr) | $SF_6$ age (yr) |
|---|---|---|---|---|---|---|---|
| | | | Date of sampling: 03 May 2001 | | | | |
| 0 | | | | 2.02 ± 0.10 | 4.18 ± 0.21 | | <0 |
| 25 | | | | 1.73 ± 0.09 | 5.22 ± 0.26 | | 4.5 ± 0.8 |
| 50 | 14.6 ± 2.3 | 4.88 ± 0.01 | 1.72 ± 0.01 | 1.84 ± 0.09 | 5.62 ± 0.28 | 8.2 ± 1.0 | 4.0 ± 0.8 |
| 75 | | | | 1.66 ± 0.08 | 6.08 ± 0.30 | | 5.5 ± 0.7 |
| 100 | | | | 1.26 ± 0.06 | 6.49 ± 0.32 | | 9.3 ± 0.6 |
| 125 | 18.9 ± 0.4 | 5.12 ± 0.02 | 2.91 ± 0.01 | 1.33 ± 0.07 | 6.31 ± 0.32 | 18.5 ± 0.3 | 8.6 ± 0.7 |
| 150 | | | | 1.16 ± 0.06 | 7.15 ± 0.36 | | 10.3 ± 0.6 |
| 175 | | | | 1.23 ± 0.06 | 6.81 ± 0.34 | | 9.6 ± 0.6 |
| 200 | 21.0 ± 0.5 | 5.31 ± 0.01 | 3.58 ± 0.01 | 1.08 ± 0.05 | 7.00 ± 0.35 | 22.0 ± 0.3 | 11.1 ± 0.6 |
| 225 | | | | 1.14 ± 0.06 | 6.70 ± 0.33 | | 10.6 ± 0.6 |
| 250 | | | | 0.99 ± 0.05 | 7.06 ± 0.35 | | 12.3 ± 0.6 |
| 283 | 21.2 ± 0.3 | 5.41 ± 0.02 | 3.68 ± 0.01 | 0.94 ± 0.05 | 6.70 ± 0.33 | 22.7 ± 0.2 | 12.8 ± 0.6 |
| | | | Date of sampling: 24 May 2005 | | | | |
| 0 | 12.2 ± 0.3 | 4.44 ± 0.03 | 1.39 ± 0.01 | 1.93 ± 0.10 | 3.15 ± 0.16 | 1.0 ± 0.3 | <0 |
| 25 | | | | 2.26 ± 0.11 | 4.87 ± 0.24 | | 3.9 ± 0.9 |
| 50 | 13.3 ± 0.6 | 4.95 ± 0.03 | 1.90 ± 0.10 | 2.19 ± 0.11 | 5.23 ± 0.26 | 11.9 ± 1.4 | 5.5 ± 0.8 |
| 75 | | | | 2.10 ± 0.10 | 5.23 ± 0.26 | | 6.1 ± 0.8 |
| 100 | 13.4 ± 0.4 | 5.06 ± 0.03 | 2.10 ± 0.02 | 2.03 ± 0.10 | 5.36 ± 0.27 | 14.9 ± 0.3 | 6.6 ± 0.8 |
| 125 | † | 5.06 ± 0.03 | 2.17 ± 0.02 | 2.28 ± 0.11 | 5.60 ± 0.28 | | 4.7 ± 0.8 |
| 150 | 13.2 ± 0.5 | 5.04 ± 0.03 | 2.16 ± 0.11 | 2.06 ± 0.10 | 5.52 ± 0.28 | 15.6 ± 1.3 | 6.4 ± 0.8 |
| 175 | | | | 2.12 ± 0.11 | 5.44 ± 0.27 | | 5.9 ± 0.8 |
| 200 | 13.5 ± 0.4 | † | † | 1.93 ± 0.10 | 5.18 ± 0.26 | | 7.4 ± 0.8 |
| 225 | | | | 2.14 ± 0.11 | 5.39 ± 0.27 | | 5.8 ± 0.8 |
| 250 | 11.8 ± 0.4 | 5.07 ± 0.03 | 1.93 ± 0.01 | 2.21 ± 0.11 | 5.06 ± 0.25 | 14.0 ± 0.4 | 5.3 ± 0.8 |
| 283 | 11.3 ± 0.7 | 5.06 ± 0.03 | 2.01 ± 0.10 | 2.18 ± 0.11 | 5.42 ± 0.27 | 15.6 ± 1.5 | 5.6 ± 0.8 |
| | | | Date of sampling: 25 Apr 2006 | | | | |
| 0 | 11.6 ± 0.4 | 4.54 ± 0.02 | 1.39 ± 0.01 | 2.36 ± 0.12 | 3.37 ± 0.17 | 1.4 ± 0.3 | <0 |
| 50 | 12.3 ± 0.4 | 5.04 ± 0.03 | 1.65 ± 0.01 | 2.46 ± 0.12 | 4.83 ± 0.24 | 9.2 ± 0.3 | 4.5 ± 0.9 |
| 100 | 12.1 ± 0.3 | 4.86 ± 0.03 | 1.78 ± 0.01 | 2.00 ± 0.10 | 4.79 ± 0.24 | 10.3 ± 0.3 | 7.9 ± 0.8 |
| 125 | 12.4 ± 0.3 | 4.92 ± 0.03 | 1.79 ± 0.01 | | | 10.8 ± 0.3 | |
| 150 | 12.8 ± 0.4 | 4.88 ± 0.03 | 1.81 ± 0.01 | 2.21 ± 0.11 | 4.60 ± 0.23 | 10.6 ± 0.3 | 6.4 ± 0.8 |
| 200 | † | 4.84 ± 0.03 | 1.83 ± 0.01 | 2.28 ± 0.11 | 4.93 ± 0.25 | | 5.9 ± 0.8 |
| 250 | † | † | † | 2.25 ± 0.11 | 4.81 ± 0.24 | | 6.1 ± 0.8 |
| 283 | 12.0 ± 0.4 | 4.90 ± 0.03 | 1.81 ± 0.01 | 2.07 ± 0.10 | 4.94 ± 0.25 | 11.1 ± 0.4 | 7.5 ± 0.8 |

* STP, standard conditions (i.e., $T_0$ 273.15 K 0°C, $p_0$ 1 atm). 1 cm³ STP 4.4615 × 10$^{-5}$ mol.
† Lost as a result of experimental problems.
, not analyzed.

ally increased during the 1990s. A first profound change in the temperature structure occurred early in 1999, when winter mixing homogenized the water temperatures from the surface to 100-m depth. At the time, the temperature of the mixed water body approached the temperature of the monimolimnion. In response to this event, a temporary increase in the $O_2$ concentrations in the uppermost 100 m was detected, but the conductivity profiles, and thus the chemical stratification of the water column, were hardly affected. However, the cooling in 1999 seems to have been of great importance for the evolution of the mixing dynamics in the following years. After 1999, vertical homogenization of the water temperatures in the uppermost 100 m occurred almost every winter, which gradually reduced the strength of the stratification in the entire lake (*see* below).

Strong changes in both temperature and electrical conductivity occurred during the winters of 2004 2005 and 2005 2006, resulting in a persistent alteration of the water column stratification. A distinct mixing event at the beginning of March 2005 led to a cooling of the deep water by ~0.3°C. The comparison of consecutive CTD profiles allowed us to estimate a duration of the mixing period of ~20 d. During this event, the distribution of dissolved solids in the water column changed dramatically. Before 2005, a strong gradient in electrical conductivity, and therefore in the concentration of dissolved solids, was present and stabilized the deep water body. The conductivity difference between 50-m and 250-m depth was 20 30 $\mu$S cm$^{-1}$. In March 2005, the electrical conductivity in the entire deep-water mass below 50-m depth was set to ~240 $\mu$S cm$^{-1}$ and remained virtually constant throughout 2005 and 2006. At the same time, traces of $O_2$ occurred at the bottom of the lake for the first time during the last ~40 yr.

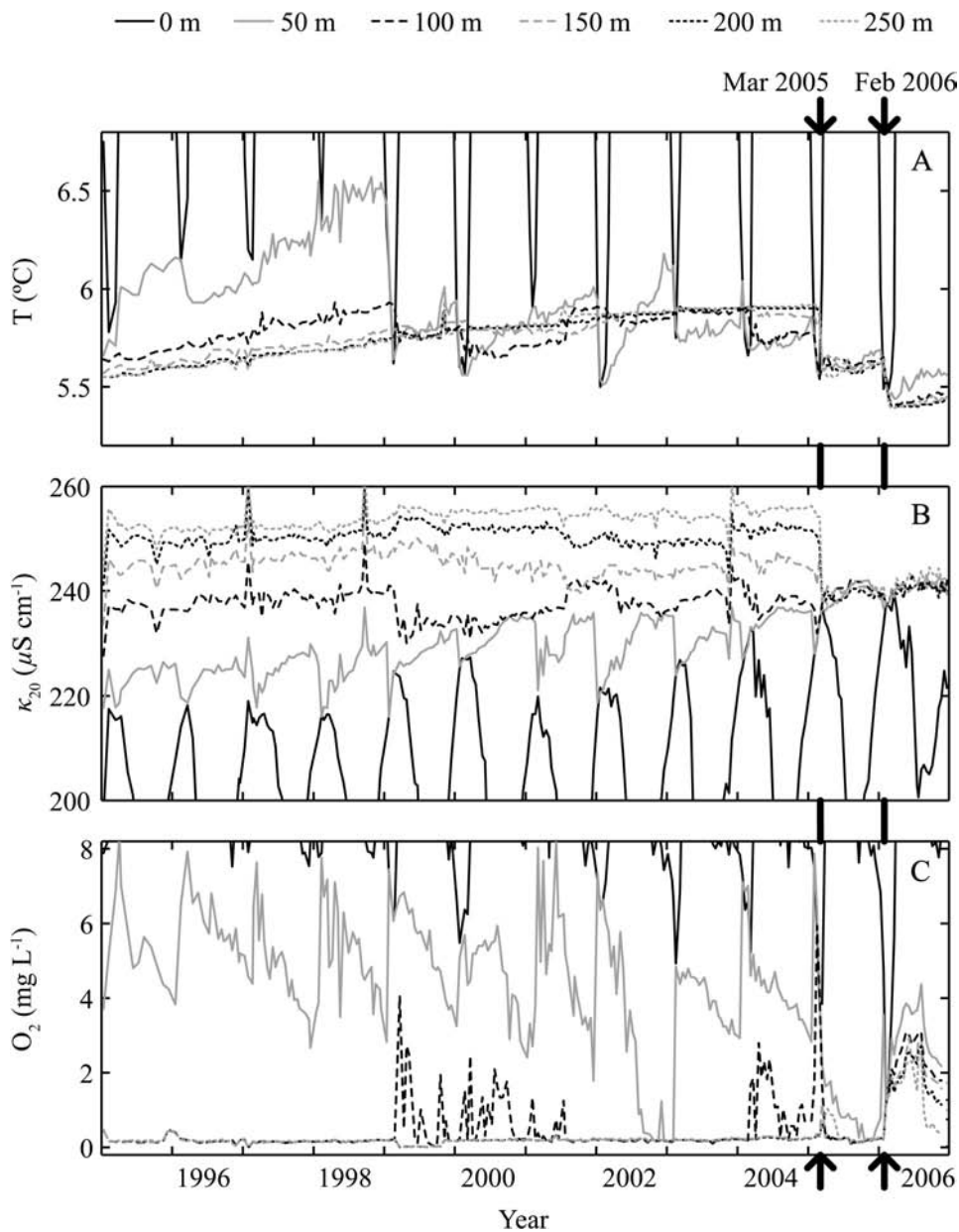A subsequent mixing event occurred at the end of January 2006 and lasted for ~60 d. It further cooled the

Fig. 2.    Temporal evolution of (A) temperature $T$, (B) electrical conductivity $\kappa_{20}$, and (C) oxygen concentration $O_2$ at selected depths. The data are from fortnightly profiles sampled in the northern basin of Lake Lugano (Fig. 1). The dates of the two recent mixing events in 2005 and 2006 are shown as vertical arrows.

deep water by an additional $\sim 0.2°C$ and resulted in nearly uniform oxygen concentrations of 1.5 2.0 mg $O_2$ L $^1$ in the entire water column. The sudden drop in $O_2$ concentration in the surface water threatened sensitive fish species. Several dead fish were discovered in Lake Lugano shortly after the mixing event (CIPAIS 2006). In the deep water, the nonzero $O_2$ concentrations prevailed until autumn, when the deepest layers turned anoxic again.

   $T$ and $\kappa_{20}$ in the water column of Lake Lugano evolved from 1995 to 2005 in a way that reduced the stratification and gradually increased the probability of mixing. An increase in the deep-water temperature during the 1990s

due to geothermal heating and turbulent diffusion has already been identified by Aeschbach-Hertig et al. (2007). The conductivity difference between the surface water and the monimolimnion of up to 30 $\mu$S cm $^1$ present before 2005 leads to a density difference that is equal to the density difference between pure water at 4°C and 5.7°C. Hence, convective mixing could occur if the surface water cools to the temperature of maximum density (i.e., $\sim 4°C$) and the monimolimnion warms above 5.7°C. The increase in the deep-water temperature continued and reached a maximal value of 5.9°C in early 2005, thus allowing the onset of convective mixing if the surface water cools sufficiently.
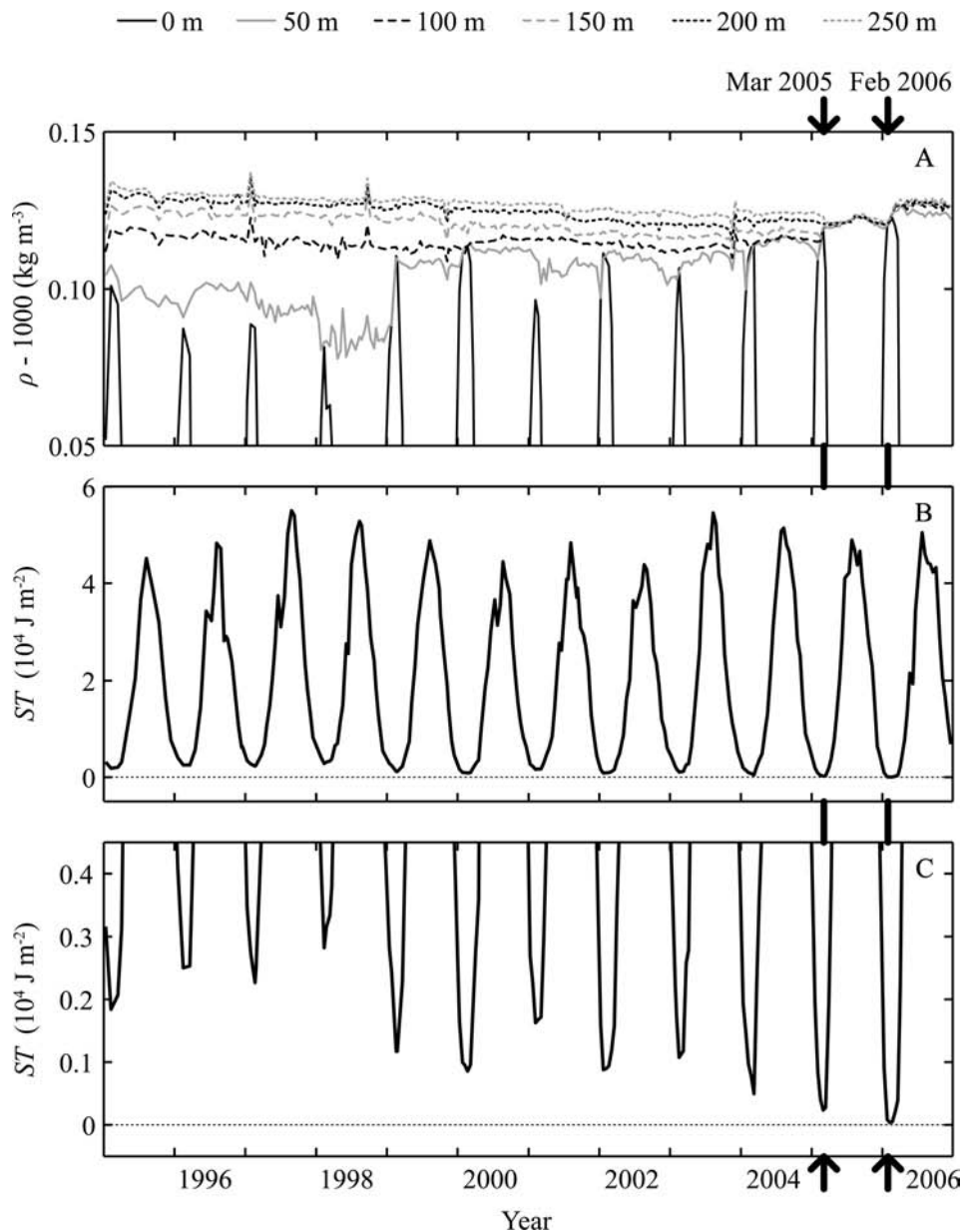
Fig. 3. Temporal evolution of (A) the water density $\rho$ at selected depths, and of (B) the Schmidt stability $ST$. (C) Enlargement of the Schmidt stability curve for $ST < 4500$ J m$^{-2}$. At $ST = 0$ J m$^{-2}$, the water column is not stratified and a minimal input of turbulent kinetic energy can trigger vertical mixing. The dates of the two recent mixing events are shown as vertical arrows.

Additionally, $\kappa_{20}$ above 100 m increased after 1999, indicating higher exchange between monimolimnion and hypolimnion, which weakened the chemical stratification. The relatively high $\kappa_{20}$ in the monimolimnion might partially be sustained by geochemical reactions facilitated by the permanent stratification. Such reactions have been identified in other meromictic lakes (Rodrigo et al. 2001). Summarizing, various events between 1995 and 2005 were responsible for reducing the vertical $T$ and $\kappa_{20}$ gradients to a point where the two consecutive cold and windy winters in 2004 2005 and 2005 2006 (CIPAIS 2005, 2006) were

finally able to initiate large-scale mixing events in Lake Lugano.

*Density and stability* The time series of the water temperature and salinity (derived from conductivity data; Wüest et al. 1992) were used to determine the density of the lake water (Chen and Millero 1986) and the stability of the water column during the last 11 yr (Fig. 3). Before the recent mixing events, the water column of Lake Lugano was characterized by a large density gradient (Fig. 3A). In February 1999 the density difference was reduced because
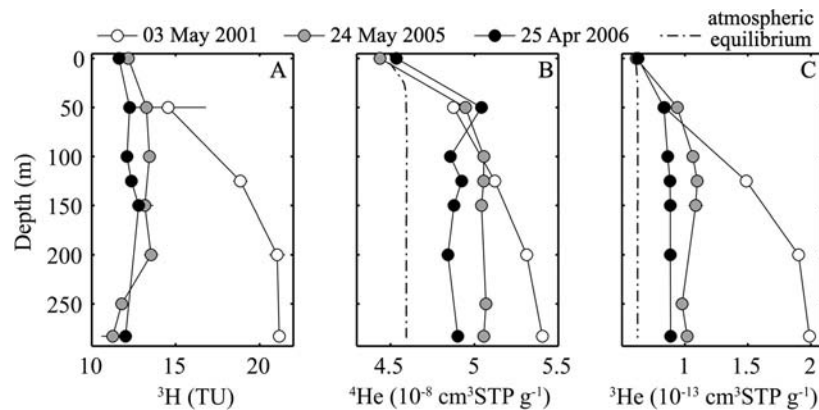
Fig. 4.   Depth profiles of (A) $^3$H, (B) $^3$He, and (C) $^4$He concentrations. Data of 2001 from Aeschbach Hertig et al. (2007). The atmospheric equilibrium concentrations for $^3$He and $^4$He are shown as broken lines.

of the cooling of the upper ~100 m, which led to a virtually homothermal state of the entire lake. However, the water column remained stratified because of the large conductivity gradient. The density gradient below 50-m depth disappeared completely after the mixing event in March 2005. In February 2006, the density of the deep water increased slightly in response to further cooling of the deep water.

To assess the evolution of the density stratification of the entire water column, we computed the Schmidt stability $ST$ (Schmidt 1928; Idso 1973) for each CTD profile (Fig. 3B). This quantity is defined as the work that would hypothetically be necessary to transform the observed density stratification into a vertically homogeneous density distribution by adiabatic mixing. A Schmidt stability value of zero means that the water column is not stratified and hence homogeneous, allowing vertical mixing to be triggered by a minimal input of turbulent kinetic energy. $ST$ is computed as follows:

$$ST = \frac{g}{A_0} \int_{z=0}^{z_{max}} [z_V - z][\rho_h - \rho(z)]A(z)\,dz \quad (Jm^{-2}) \quad (1)$$

where $g$ is the acceleration of gravity (9.81 m s $^{-1}$), $A_0$ is the surface area of Lake Lugano ($2.75 \times 10^7$ m$^2$), $z_{max}$ is the maximum depth of the lake (288 m), $z_V$ is the depth of the center of volume of the lake (171 m), $\rho_h$ is the hypothetical density of the homogeneous lake after mixing, $\rho(z)$ is the observed density at depth $z$, and $A(z)$ is the isobath area at depth $z$. The Schmidt stability in Lake Lugano shows an annual cycle with the lowest values occurring in winter, when vertical density gradients are low because of seasonal cooling at the surface. Since 1995, the minimum Schmidt stabilities observed in winter (Fig. 3C) decreased substantially. A remarkable drop in the minimum Schmidt stability took place in February 1999, after the change in water temperatures shown in Fig. 2A. After 1999, cooling of the surface water below the temperature of the monimolimnion caused an unstable thermal stratification of the water column during winter. However, a stable density stratification due to the concentration gradient of dissolved solids (reflected in conductivity) was present throughout that time

and suppressed large-scale vertical water exchange. The ongoing warming of the deep water and a slight increase in the conductivity of the surface water (Fig. 2A,B) after 1999 gradually reduced the stratification in winter until the Schmidt stability approached zero during the winters of 2004 2005 and 2005 2006, and seasonal mixing homogenized the water column.

*Transient tracer concentrations*   Figure 4 shows the concentrations of $^3$H, $^3$He, and $^4$He in the water column of Lake Lugano during spring 2001, 2005, and 2006. The corresponding concentration profiles of SF$_6$ and CFC-12 are presented in Fig. 5. The tracer data are listed in Table 1.

In 2001, the $^3$H concentrations increased continuously with depth. This profile reflects the high $^3$H input to the lake in the 1960s and 1970s from rivers and precipitation as a result of thermonuclear bomb tests in the atmosphere. As Lake Lugano became permanently stratified because of eutrophication at the time of high $^3$H input, high concentrations of $^3$H were stored in the monimolimnion and decayed continuously to $^3$He. As a consequence, the tritiogenic $^3$He that was generated accumulated in the monimolimnion. In the surface water, the $^3$H concentrations were also reduced by mixing with new inflow water that contained lower $^3$H concentrations, and by exchange with atmospheric water vapor. The $^3$H concentration profiles observed in 2005 and 2006 do not show substantial variation with depth. In the monimolimnion, the concentrations are considerably lower than in 2001. The maximum $^3$H concentrations near the bottom decreased from ~21 tritium units (TU, where 1 TU = 1 $^3$H atom 10$^{18}$ $^1$H atoms $^{-1}$) in 2001 to 11 12 TU in 2005 and 2006. Note that the $^3$H concentrations measured in 2005 and 2006 are significantly below the concentrations that would be expected if radioactive decay were the only process to remove $^3$H from the deep water (16 17 TU). Therefore, the exchange with $^3$H-poor surface water during the mixing events significantly reduced the observed $^3$H concentrations in the deep water. During the 1990s, the $^3$H concentrations in the monimolimnion of Lake Lugano were already decreasing faster than expected because of the process of
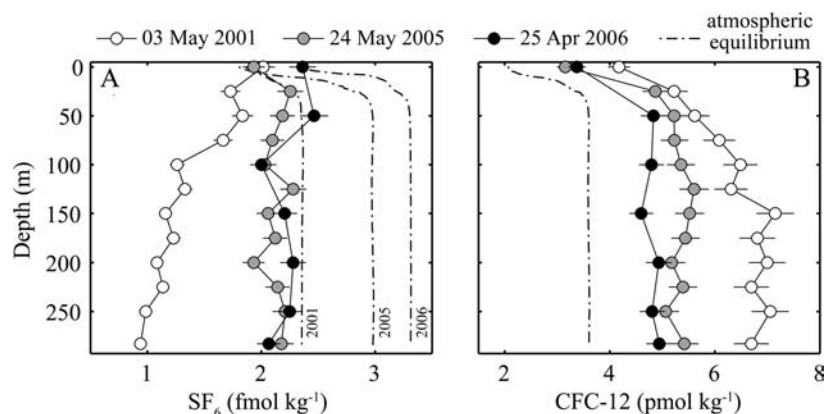
Fig. 5. Depth profiles of (A) $SF_6$ and (B) CFC 12 concentrations. Data of 2001 from Aeschbach Hertig et al. (2007). The atmospheric equilibrium concentrations for $SF_6$ and CFC 12 are shown as broken lines. Note the transient evolution of the $SF_6$ equilibrium concentrations caused by the continuous increase in atmospheric $SF_6$ concentrations.

radioactive decay alone (Aeschbach-Hertig et al. 2007). An exponential fit to the data from 1990 to 2001 yields a removal rate of 0.077 yr$^{-1}$, which is higher than the radioactive decay rate of $^3H$ (0.056 yr$^{-1}$). However, this rate is considerably lower than the rate of 0.133 yr$^{-1}$ that was determined by fitting the data from 2001 to 2006, during which the strong mixing events occurred. This implies that the monimolimnion of Lake Lugano was not completely isolated before 2005, and that turbulent mixing caused a significant exchange with the hypolimnion. But this turbulent water exchange rate was considerably smaller than the convective deep-water renewal rate in 2005 and 2006.

In all profiles, $^3He$ and $^4He$ in the deep water are supersaturated with respect to gas-partitioning equilibrium with the atmosphere. The He excess is caused by the accumulation of tritiogenic $^3He$ (produced by $^3H$ decay) and terrigenic $^4He$ (emanating from the solid earth through the sediments) in the monimolimnion. Our earlier work (Aeschbach-Hertig et al. 2007) documented a continuous increase in the $^4He$ concentrations of the deep water of Lake Lugano during the 1990s and a slight decrease in the $^3He$ concentrations since 1992. In contrast, the helium concentrations below ~50 m decreased strongly between 2001 and 2005 and between 2005 and 2006. These changes indicate that the mixing events transported part of the excess He from the deep water to the surface, where it escaped to the atmosphere. A budget of excess He stored in the northern basin of Lake Lugano was calculated from interpolated profiles by integrating the product of the excess concentration $C^{ex}(z)$ with the bathymetric area $A(z)$ over depth $z$. The excess concentration is given as $C^{ex}(z) = C(z) - C^{eq}(z)$, where $C(z)$ is the observed noble gas concentration and $C^{eq}(z)$ is the atmospheric equilibrium concentration at depth $z$. These calculations allowed us to estimate the mass of excess He in the lake from each concentration profile; e.g., ~40 mg of excess $^3He$ and ~4 kg of excess $^4He$ in 2001. In comparison, the total dissolved masses of He in 2001 were ~80 mg of $^3He$ and ~40 kg of $^4He$. The mass balance shows also that ~48% of the excess $^3He$ and ~16% of the excess $^4He$ degassed to the

atmosphere between 2001 and 2005. From 2005 to 2006, the remaining excess of $^3He$ and $^4He$ decreased by a further ~39% and ~23%, respectively. The relative loss of $^3He$ is much higher than the loss of $^4He$ because in 2001 $^3He$ was much more highly supersaturated than $^4He$.

The $SF_6$ concentrations observed in 2001 decreased from the surface to the bottom of the lake because of gas exchange with the atmosphere and in response to the continuously increasing atmospheric $SF_6$ partial pressure (Maiss and Brenninkmeijer 1998), and because of the limited vertical water exchange in Lake Lugano. In contrast, the $SF_6$ concentrations observed in 2005 and 2006 were nearly constant throughout the water column, again indicating extensive mixing and homogenization of the water column. The mixing events in March 2005 and February 2006 led to an increase in the $SF_6$ concentrations in the entire lake due to gas exchange with the increasingly "$SF_6$-rich" atmosphere. However, the $SF_6$ concentrations in the water column remained below the atmospheric equilibrium concentration, especially in the colder deep water, because the mixing events were too short to allow gas-partitioning equilibrium to be attained throughout the lake.

The deep water of Lake Lugano has been supersaturated with respect to CFC-12 for several years, presumably due to contamination (Aeschbach-Hertig et al. 2007). In 2001, the excess of dissolved CFC-12 in the lake water body was ~1.5 kg. This quantity of CFC-12 may have been introduced into Lake Lugano by accident or due to inappropriate disposal, as CFC-12 was widely used as cooling fluid in refrigerators and air conditioners before it was banned by the Montreal Protocol (Ozone Secretariat 2000). The reduction in CFC-12 concentrations that occurred from 2001 to 2006 is the result of the increased upward transport of deep water rich in CFC-12, and the subsequent loss of CFC-12 to the atmosphere by gas exchange at the lake surface.

## Discussion

*Apparent water ages* The apparent water ages derived from the $^3H$, $^3He$, and $SF_6$ data for 2001, 2005, and 2006
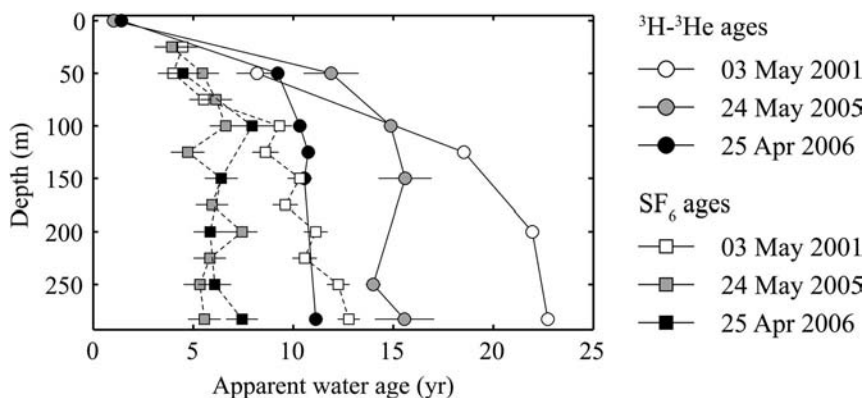
Fig. 6.    Depth profiles of the apparent $SF_6$ and $^3H$ $^3He$ ages. Apparent tracer ages of 2001 from Aeschbach Hertig et al. (2007).

are shown in Fig. 6 and Table 1. CFC-12 cannot be used to determine water ages in Lake Lugano, because the observed concentrations exceed the atmospheric equilibrium concentration. In 2001, both the ages calculated from $^3H$-$^3He$ and from $SF_6$ increased considerably with depth, which indicates that vertical mixing in the water column was slow. However, the mixing events led to a distinct decrease in the apparent water ages in the deep water and to a reduction in the age difference between surface and deep water. The apparent $^3H$-$^3He$ age close to the bottom of the lake decreased from ~23 yr in 2001 to ~16 yr in 2005 and ~11 yr in 2006. The apparent $SF_6$ age dropped from ~13 yr in 2001 to 6 7 yr in 2005 and 2006. Hence both the $^3H$-$^3He$ age and the $SF_6$ age were reduced by ~50%, indicating considerable deep-water renewal.

SF$_6$ ages are systematically lower than $^3H$-$^3He$ ages over the entire study period. The difference between the apparent water ages determined using different tracers is caused by the nonlinear effect that mixing has on water age (Hofer et al. 2002; Kipfer et al. 2002; Vollmer et al. 2002). The mixture of two water volumes with different ages should ideally have the volume-weighted mean age; i.e., the "true" water age. However, mixing generates water containing volume-weighted mean tracer concentrations. As the tracer ages are nonlinear functions of the tracer concentrations, the tracer age of the mixed water may deviate significantly from the "true" water age. The effect of mixing on tracer age depends on the tracer used for dating, the date of sampling, and the water age of the mixed water bodies. Aeschbach-Hertig et al. (2007) simulated the evolution of the apparent tracer ages in Lake Lugano over the last century using a simple mixed-reactor model. This analysis showed that $SF_6$ ages appear to underestimate the true water age, whereas $^3H$-$^3He$ ages seem to overestimate it. Therefore, the true water age in Lake Lugano lies between the apparent $SF_6$ and $^3H$-$^3He$ ages, and is not well constrained given the large differences in tracer ages. For this reason, to estimate the vertical water exchange that occurred during the recent mixing events we use the observed tracer concentrations rather than the water ages.

*Quantification of deep-water renewal*    On the basis of the mass balance of $^3He$ below 100-m depth, Aeschbach-Hertig et al. (2007) determined that between 1990 and 2001 about 8% of the deep water was exchanged with surface water annually. This relatively small renewal rate reflects the effect of the permanent stratification that prevailed before 2005, which limited vertical water exchange. Using the same $^3He$ mass balance approach for the time intervals 2001 2005 and 2005 2006 yields deep-water renewal rates of ~75% per year and ~270% per year, respectively. As expected, during these periods the deep-water renewal rates are considerably higher than those observed before 2001. However, the resulting rates cannot be directly related to the convective water exchange during the actual mixing events, because the approach used here yields mean exchange rates for the entire periods between successive samplings. As the time periods analyzed are much longer than the observed mixing events, the resulting rates appear considerably smaller than the effective water turnover during the mixing events in 2005 and 2006.

To better constrain the deep-water renewal that occurred during the mixing events in 2005 and 2006, we developed a dynamic three-box model for the northern basin of the lake (Fig. 7). The model simulates the temporal evolution of $^3H$, $^3He$, $^4He$, and $SF_6$ concentrations in the lake from 1990 to 2007, taking into account the processes of gas exchange at the water surface, tracer gain or loss due to water inflow and outflow, vertical water transport, $^3He$ production by the radioactive decay of $^3H$, and terrigenic He input. The model was set up and numerically integrated using the simulation software AQUASIM (Reichert 1994). The basin of Lake Lugano is modeled as three horizontal layers (epilimnion, hypolimnion, and monimolimnion) representing zones of different mixing intensity. The epilimnion is assumed to be well mixed by wind and undergoes gas exchange with the atmosphere. The hypolimnion undergoes seasonal mixing, whereas the monimolimnion corresponds to the deep water body that was permanently stratified before 2005. The three layers are modeled as mixed reactors, connected by water flows that represent the vertical transport processes.

Our main interest is focused on vertical transport during the mixing events in 2005 and 2006, expressed as water flows of equal magnitude between the epilimnion and the hypolimnion as well as between the hypolimnion and the
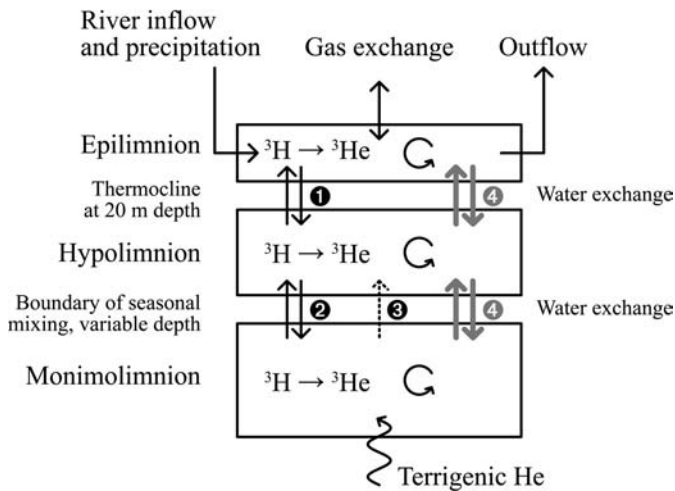
Fig. 7. Illustration of the three box model of Lake Lugano. The vertical water exchange flows are labeled as follows: (1) turbulent water exchange across the thermocline; (2) weak renewal of the monimolimnion water (8% per year before 2005); (3) water flow that compensates for the deepening of the boundary between the hypolimnion and the monimolimnion boxes; (4) large vertical exchange during the mixing events in 2005 and 2006.

monimolimnion, which occur only during the observed mixing periods. Apart from this exceptional water exchange, the model also accounts for the turbulent exchange across the thermocline described by a constant exchange rate between the epilimnion and the hypolimnion (of 60% of the hypolimnion volume per year; Dzambas and Ulrich 1994). Correspondingly, before 2005, for the monimolimnion a water renewal rate of 8% per year (exchanged with water from the hypolimnion) was assumed (Aeschbach-Hertig et al. 2007). The duration of the mixing events, the depth of the thermocline (considered to be the boundary between epilimnion and hypolimnion), and the depth of the boundary between the hypolimnion and the monimolimnion were estimated from the time series of CTD profiles from 1995 to 2005. We assumed that the epilimnion corresponds to the surface layer that becomes warmer than 10°C in summer. Applying this criterion, the thermocline

depth remained virtually constant at about 20 m, the value used in the model. The maximum depth of seasonal mixing, i.e., the boundary between the hypolimnion and the monimolimnion, is assumed to correspond to the maximum depth at which oxygen is detected during regular lake monitoring in a particular year. This depth gradually increased from 85 m in 1995 to 110 m in 2004. In the model, the depth of the boundary increases with time at a constant rate. It results in a corresponding upward net water flow from the hypolimnion to the monimolimnion box.

We used the tracer data given in Table 1 and earlier data (Aeschbach-Hertig et al. 2007) to constrain the model parameters. For each box, we calculated volume-weighted mean concentrations of the tracers from interpolated profiles. The 1990 data were used as initial conditions. The inverse fitting tools of AQUASIM were applied to tune the gas exchange velocities of He and $SF_6$ across the air water interface and to estimate the vertical water transport during the mixing events in 2005 and 2006.

The modeled histories of $^3H$ and $^3He$ are in reasonably good agreement with the tracer measurements (Fig. 8). In particular, the dramatic changes in the tracer concentrations during the mixing events in 2005 and 2006 are adequately reproduced. For $^4He$ and $SF_6$ the model results (not shown) deviate from the observations, because the input of these tracers into Lake Lugano cannot be adequately reconstructed. Beside solubility disequilibria due to fast warming of the surface water, Aeschbach-Hertig et al. (2007) also propose that elevated $SF_6$ concentrations in the local air might explain the slight supersaturation with respect to $SF_6$ found for the surface sample in 2001. However, the magnitude and temporal evolution of the proposed atmospheric $SF_6$ excess remains unclear and cannot be appropriately modeled. The terrigenic input of $^4He$ into lakes depends on the underlying geological structures and may be spatially nonuniform (Mamyrin and Tolstikhin 1984; Ballentine and Burnard 2002; Brennwald 2004). A clear allocation of the terrigenic $^4He$ input to each of the three boxes of the model is therefore not possible, leading to uncertainties in the modeled $^4He$ evolution.
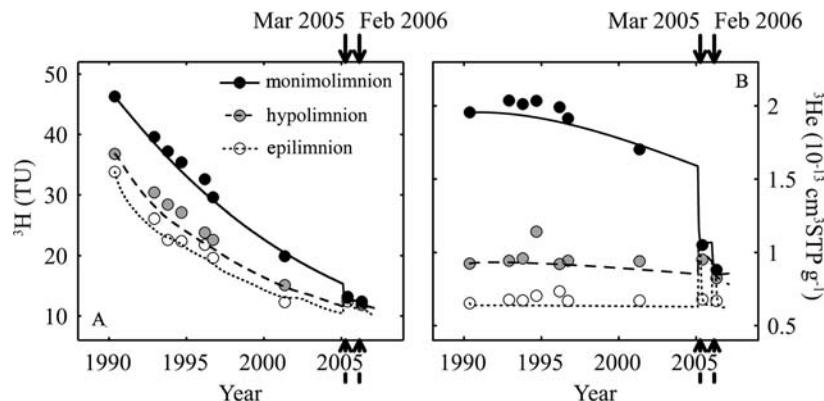


Fig. 8. Results of the three box model calculations. (A) Measured and modeled $^3He$ concentrations. (B) Measured and modeled $^3H$ concentrations. Tracer data are from Aeschbach Hertig et al. (2007) and this study. The dates of the two recent mixing events are shown as vertical arrows.

Table 2. Results of the three box model. The total volumes of water exchanged and the gas exchange velocities were determined using inverse fitting methods.

**Deep water renewal**

| Year | $V_{ex}$ (m³) | $V_{ex} : V_m$ |
|------|------------|-------------|
| 2005 | $(6 \pm 4) \times 10^9$ | $2.3 \pm 1.4$ |
| 2006 | $(17 \pm 11) \times 10^9$ | $6.8 \pm 4.3$ |

**Gas exchange velocities $v_i$ (m d⁻¹)**

| Gas $i$ | Modeled* | Empirical** |
|---------|----------|-------------|
| SF$_6$ | 0.23 | 0.16 |
| ³He | 0.84 | 0.64 |
| ⁴He | 0.76 | 0.58 |
| O$_2$ | 0.32 | 0.24 |

$V_{ex}$, water exchanged during the mixing events, estimated using inverse fitting.

$V_m$, mean volume of the monimolimnion box ($2.5 \times 10^9$ m³).

* The gas exchange velocity for SF$_6$ is estimated in the model using inverse fitting. The other velocities are calculated using $v_i : v_j$ $(D_i : D_j)^{2/3}$ (Schwarzenbach et al. 2003). Estimated errors in the gas exchange velocities are $\pm 10\%$.

** Empirical gas exchange velocities $v_i$ are calculated according to Wanninkhof (1992) for the mean wind speed measured at the MeteoSwiss station in Lugano in the period from 1971 to 2000 (1.75 m s⁻¹) and for the mean annual surface water temperature from the CTD measurements (14°C).

The total water volumes exchanged during the mixing events and the corresponding gas exchange velocities for He and SF$_6$ are summarized in Table 2. Note that the mixing events of 2005 and 2006 are characterized by exchanged water volumes that exceed the volume of the monimolimnion by factors of about two and seven, respectively. As expected, these rates are considerably higher than the ones determined using a simple mass balance of ³He for the deep water (*see* above). The fairly large uncertainties are due to the fact that the tracer concentration gradients below 50-m depth become virtually zero during the mixing events, making the outcome of the model only weakly dependent on the vertical water exchange.

The estimated gas exchange velocities (Table 2) are about 30–40% higher than the velocities calculated from the mean wind speed measured at the meteorological station in Lugano and the mean annual surface water temperature of the lake using an empirical relationship (Wanninkhof 1992). These differences are likely due to the fact that the effective wind speeds on the lake are significantly higher than those measured in Lugano. Furthermore, gas exchange velocities calculated using the mean wind speed tend to underestimate the actual exchange because of the nonlinear effect of wind-speed variability on gas transfer (Livingstone and Imboden 1993). We used the estimated gas exchange velocity for SF$_6$ to calculate the corresponding velocity for O$_2$. Combined with the $T$ and O$_2$ data from the CTD measurements (*see* Fig. 2), our estimate of the O$_2$ gas exchange velocity can be used to calculate the flux of O$_2$ into the northern basin of Lake Lugano. For instance, during the second mixing event in February 2006, which lasted ~60 d, about $8 \times 10^4$ kg of O$_2$ per day were injected into the lake. This input corresponds to a concentration increase of only ~1 mg L⁻¹ O$_2$ for the entire lake volume. Consequently, the O$_2$ concentrations in the entire water column remained low (<5 mg L⁻¹) until the onset of stratification in April 2006 because of the continuing mixing and fast O$_2$ consumption by the large reservoir of reducing substances in the deep water (Barbieri and Mosello 1992; UPDA 2006).

*Transition in the mixing dynamics* The transient tracer profiles and the time series of CTD data from Lake Lugano record substantial changes in the physical and chemical properties of the water column in response to two strong convective mixing events during the winters of 2004–2005 and 2005–2006. Before 2005, the deep water of Lake Lugano had been permanently stratified for ~40 yr and the physical and chemical state of this water body had undergone only minor changes due to limited turbulent transport. Turbulent diffusion and geothermal heating gradually warmed the deep water over the last decade and reduced the conductivity gradient in the water column slightly. This evolution reduced the strength of the stratification to a point where a large-scale convective mixing event ("overturn") of the entire water column was able to take place. The onset of the recent mixing events in Lake Lugano was favored by exceptionally cold and windy conditions that had occurred during the preceding winters. The considerable deep-water renewal (a vertical water exchange that exceeds the monimolimnion volume) and extensive gas exchange that occurred in 2005 and 2006 is clearly documented by transient tracer concentrations, obtained immediately after the two mixing events, which differ substantially from earlier data.

The environmental tracer data collected for this work, along with previously published data (Aeschbach-Hertig et al. 2007), form a 15-yr time series of tracer measurements in the northern basin of Lake Lugano. These data provide a record of the mixing dynamics of the lake from 1990–2006. During this period, the deep-water renewal rates in the lake increased by a factor greater than 10 because of the two strong winter mixing events. Our work demonstrates that long time series of environmental tracer data are useful for analyzing transitions in the mixing regimes of lakes in response to environmental and climatic changes. For this purpose, the time period covered by a tracer study needs to be long enough to cover typical timescales of the mixing dynamics that are representative of the particular lake concerned.

Compared with dissolved oxygen concentrations or with the temperature and conductivity of the lake water, the effects of mixing on the environmental tracer concentrations (noble gases, SF$_6$, and CFCs) are more pronounced and the resulting tracer signals are detectable over a longer time, because these tracers are biochemically conservative in lakes. Transport within the lake and gas exchange with the atmosphere are therefore the main processes that affect the observed tracer concentrations and the data collected are suitable for quantifying the corresponding process rates. As an example, lake monitoring on the basis of noble gas analyses allows the exchange of dissolved gases with the anoxic deep water during a mixing event to be documented,

whereas oxygen cannot be used as a tracer because of the fast oxygen consumption.

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