The physical structure and dynamics of a deep, meromictic crater lake (Lac Pavin, France)

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Abstract

The characteristic feature of the physical structure of Lac Pavin is a distinct and permanent chemically induced density increase between about 60 and 70 m depth. This chemocline separates the seasonally mixed mixolimnion from the monimolimnion, which is characterized by elevated temperature and salinity as well as complete anoxia. Previously published box-models of the lake postulated substantial groundwater input at the lake bottom, and consequently a short water residence time in the monimolimnion and high fluxes of dissolved constituents across the chemocline. We present a new view of the physical structure and dynamics of Lac Pavin, which is based on the results of high-resolution CTD profiles, transient and geochemical tracers (tritium, CFCs, helium), and numerical modeling. The CTD profiles indicate the existence of a sublacustrine spring above rather than below the chemocline. A stability analysis of the water column suggests that vertical turbulent mixing in the chemocline is very weak. A numerical one-dimensional lake model is used to reconstruct the evolution of transient tracer distributions over the past 50 years. Model parameters such as vertical diffusivity and size of sublacustrine springs are constrained by comparison with observed tracer data. Whereas the presence of a significant water input to the monimolimnion can clearly be excluded, the input to the mixolimnion – both at the surface and from the indicated sublacustrine spring – cannot be accurately determined. The vertical turbulent diffusivity in the chemocline is well constrained to $K \approx 5 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$, about a factor of three below the molecular diffusivity for heat. Assuming thus purely molecular heat transport, the heat flow through the chemocline can be estimated to between 30 and 40 mW m^{-2} . With respect to dissolved constituents, the very weak turbulent diffusive exchange is equivalent to a stagnant monimolimnion with a residence time of nearly 100 years. Based on these results and vertical concentration profiles of dissolved species, diffusive fluxes between monimolimnion and mixolimnion can be calculated. A large excess of helium with a $^3\text{He}/^4\text{He}$ ratio of $(9.09 \pm 0.01) \times 10^{-6}$ ($6.57 R_a$) is present in the monimolimnion, clearly indicating a flux of magmatic gases into the monimolimnion. We calculate a flux of $1.0 \times 10^{-12} \text{ mol m}^{-2} \text{ s}^{-1}$ for mantle helium and infer a flux of $1.2 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$ (72 t year^{-1}) for magmatic CO_2 . The monimolimnion appears to be in steady state with respect to these fluxes.

Introduction

The peculiar physico-chemical properties of Lac Pavin have attracted a considerable scientific interest in this

small lake. Pelletier (1968) first described the existence of a monimolimnion – a deep water body not affected by seasonal vertical mixing – below about 60 m depth in the 92 m deep crater lake. By now it

is firmly established that Lac Pavin is meromictic, i.e., that the monimolimnion is a permanent feature. Due to high concentrations of dissolved ions this deep water is denser than the water of the overlying mixolimnion – the seasonally mixed layer – despite its elevated temperature. The monimolimnion is permanently anoxic and has elevated concentrations of gases such as CO₂ and CH₄ (Camus et al., 1993) as well as of many trace elements (Viollier et al., 1995).

A second peculiarity of Lac Pavin is that surface water inputs and outputs are apparently not balanced. The existence of sublacustrine springs was suggested to account for the missing water input (Glangeaud, 1916; Meybeck et al., 1975). Tritium data have repeatedly been used to assess the water balance. Alvinerie et al. (1966) found no evidence for a spring in the first tritium profiles from the lake. Meybeck et al. (1975) postulated a spring of mineralized water discharging into the monimolimnion, which would explain the origin of the monimolimnion and close the water balance. Martin (1985) used a box-model based on tritium data to quantify the discharge of the spring. In a study assessing the potential risk of catastrophic CO₂ degassing at Lac Pavin, Camus et al. (1993) concluded that the high CO₂ concentrations in the monimolimnion were entirely biogenic. They reassessed the box-model and confirmed the presence of a spring in the monimolimnion, but concluded from geochemical evidence that it was not strongly mineralized. Their model was used in subsequent geochemical studies to calculate element fluxes through the chemocline (Michard et al., 1994; Viollier et al., 1995). Due to the substantial deep spring in this model, the water residence time in the monimolimnion is short and upward advective fluxes are large.

Based on our experience with volcanic lakes (Kipfer et al., 1994; Aeschbach-Hertig et al., 1996b) as well as permanently stratified lakes (Wüest et al., 1992; Aeschbach-Hertig, 1994) we doubted the correctness of the mentioned views on both the origin of the dissolved gases in the monimolimnion and the residence time of the water. The basis of an assessment of the physical structure of a lake must be a precise determination of temperature, conductivity and density profiles. High resolution CTD (conductivity, temperature, depth) profiling may yield indications of the presence of sublacustrine springs. Transient tracers such as the ³H–³He isotope pair or chlorofluorocarbons (CFCs) provide direct information on the time scales of mixing in lakes (e.g., Torgersen et al., 1977; Weiss et al., 1991; Aeschbach-Hertig et al., 1996a;

Kipfer et al., 2002). The full potential of these methods is reached if they are combined with numerical lake models to determine physical parameters such as the vertical turbulent diffusion coefficient by inverse modeling (Peeters et al., 1997a).

Therefore, we applied all these methods of modern physical limnology to determine the mixing characteristics of Lac Pavin. Preliminary evaluation of some of these data (Schmid, 1997) showed that the tritium results can also be explained with a spring in the mixolimnion and very slow diffusive exchange across the chemocline. Aeschbach-Hertig et al. (1999a) showed that the He data are inconsistent with the hypothesis of a spring in the monimolimnion, but in accordance with a uniform He flux from the sediment and a long residence time in the monimolimnion. Independently, Viollier et al. (1997) dismissed the existence of a spring in the monimolimnion based on element fluxes observed in sediment traps. Whereas the residence time in the monimolimnion was estimated to about 3 years in the old models with a deep spring, the new models suggest a residence time of the order of 100 years.

This study presents a detailed discussion of the present view of the physical structure and dynamics of Lac Pavin, which involves a sublacustrine spring above rather than below the chemocline and a long residence time of the water in the monimolimnion, based on CTD and tracer data and a numerical lake model. The presented results provide the necessary physical background for the correct interpretation of chemical and biological data from Lac Pavin. They may yield further benefits if they are combined with the considerable body of geochemical data acquired at Lac Pavin by other investigators. As an example, we use the model to quantify the fluxes of He and CO₂ into the lake. The present work focusing on the physical limnology of Lac Pavin complements the previously published geochemical study (Aeschbach-Hertig et al., 1999a).

2. Methods

On the occasion of a first exploration at Lac Pavin in August 1993, three water samples for He isotope and tritium analysis were taken with the most elementary methods. A Niskin bottle on a rope was lowered by hand from a small rowing boat. Temperature was measured with a thermometer after recovery of the bottle. During two expeditions in September 1994 and

1996, high resolution CTD profiles were recorded with a Seacat SBE-19 probe, which was also equipped with sensors for dissolved oxygen, pH, and light transmissivity. Furthermore, profiles of water samples were taken using Niskin samplers and a hand-driven winch. Samples were taken in copper tubes for gas (He, Ne, CFCs, CH₄, N₂, Ar) and tritium analyses, in glass or PET bottles for later Winkler titration on shore as well as for determination of alkalinity, major ions, and tritium in the laboratory.

The Seacat SBE-19 CTD probe records data twice per second, and was lowered slowly to obtain readings every 10–20 cm. It measures temperature with an accuracy of 0.01 °C and a resolution of 0.001 °C. The resolution for the electrical conductivity is better than 1 $\mu\text{S cm}^{-1}$. Dissolved oxygen is measured with an accuracy of about 0.1 mg l⁻¹, and pH is accurate to about 0.1 units. However, the oxygen and pH sensors are subject to long-term drifts that require regular calibration. The oxygen sensor was calibrated against the results of Winkler measurements on water samples, and the pH sensor was calibrated with standard buffer solutions. Both sensors have a relatively high response time, which may lead to some distortions of the profiles in the presence of very sharp gradients. For the horizontal CTD survey in 1996, the position on the lake was measured by means of a theodolite on shore, allowing precise determination of distance and angle relative to a reference point.

For the gas analyses, the water was transferred into copper tubes immediately after recovery from the lake and tightly sealed off by stainless steel clamps on both ends. This standard sampling procedure was problematic for the very gas-rich samples from the deepest part of Lac Pavin. Samples taken from below about 70 m depth showed a tendency to degas, observable as bubbles forming in the transparent tubing used for the transfer of the water to the copper tubes. Such degassing indicates the presence of high concentrations of dissolved gases, most likely CO₂ or CH₄, which exsolve due to the reduction of hydrostatic pressure during sampling. No special measures were taken to avoid degassing or to collect the exsolving gas, but the measured concentrations can be corrected for the effect of degassing (Aeschbach-Hertig et al., 1999a). The atmospheric equilibrium concentrations for all gases were calculated as outlined by Aeschbach-Hertig et al. (1999b) using the respective literature solubility data, the measured temperature and salinity, and an atmospheric pressure of 0.87 atm, corresponding to the altitude of Lac Pavin of 1197 m.

He, Ne and tritium were analyzed in the ETH noble gas mass spectrometry laboratory according to the procedures described by Beyerle et al. (2000). The dissolved gases were extracted from the water under vacuum and admitted to a purification line to separate the He and Ne fractions. He and Ne were then analyzed for concentration and isotopic composition in two non-commercial mass spectrometers. Calibration was performed relative to an air standard. The average 1 σ -errors of the samples from Lac Pavin are 0.4% for the ³He/⁴He ratios, 0.6% for the ⁴He concentrations, and 1.0% for the Ne concentrations. These values are close to the long-term mean reproducibility of the system, as derived from regular analyses of aliquots of an internal freshwater standard. Tritium was measured by the ³He ingrowth technique (Clarke et al., 1976). To accumulate ³He from the tritium decay, the water which had previously been degassed for the He and Ne analysis was stored for several months in the same copper tubes. The accuracy of the tritium measurements is usually a few percent.

The high ³He concentrations in the monimolimnion of Lac Pavin gave rise to an unusual problem with the ingrowth method of tritium analysis. Although the gas extraction for the He and Ne analysis reduced the ³He content of the samples by at least four orders of magnitude, still a detectable rest of ³He remained in the water, which interfered with the later measurement of the tritiogenic ³He. This residual ³He was corrected by using the total ⁴He amount measured in the tritium analysis and the ³He/⁴He ratio from the prior He analysis. The correction somewhat enlarged the uncertainty of the tritium concentrations in the monimolimnion. In order to obtain faster and more precise tritium results, several large ($\approx$ 1 kg) water samples were thoroughly degassed and stored for some weeks in stainless steel bulbs. However, even these samples had to be corrected for residual He.

CFC-11 (CFCl₃) and CFC-12 (CF₂Cl₂) were analyzed at EAWAG on a gas chromatograph equipped with an electron capture detector, as described by Hofer & Imboden (1998). CH₄, N₂, and Ar were measured on the same GC system with a thermal conductivity detector. Calibration was performed with an air standard, and accuracy is on the order of a few percent. Detection limits are 0.01 and 0.02 pmol kg⁻¹ for CFC-11 and CFC-12, respectively. The samples taken in copper tubes in 1994 for the analysis of CFCs were stored for 2 years and measured together with the samples from 1996 shortly after that expedition. Since CFCs, particularly CFC-11, can be degraded

Figure 1. Profiles recorded with the CTD probe near the center of Lac Pavin on 20 September 1994 and 10 September 1996. (a) Temperature. Also shown is the temperature of maximum water density (T_{md}) as a function of depth. Insert: Water column below 20 m on enlarged temperature scale. (b) Electrical conductivity normalized to 20 °C (κ_{20}). Insert: Mixolimnion on enlarged scale. (c) Dissolved oxygen. Points mark values obtained from Winkler samples, which were used to calibrate the sensor on the CTD probe. Insert: Water column between 25 and 55 m on enlarged scale.

during storage in the copper tubes (Hofer & Imboden, 1998), the results from 1994 have to be interpreted with caution.

3. Results

3.1. Temperature, conductivity, and dissolved oxygen

From the main large scale features of the central vertical profiles of temperature, electrical conductivity, and dissolved oxygen, three relatively uniform layers of water and two interfaces can be clearly distinguished (Fig. 1):

- (1) The epilimnion, or surface mixed layer, with a seasonally varying temperature and depth. At the times of our main sampling campaigns, in September 1994 and 1996, the epilimnion was about 10 m deep and had a temperature of 12.6 and 14.5 °C, respectively. Oxygen concentrations were close to atmospheric equilibrium.
- (2) The thermocline, characterized by a steep temperature gradient. The thermocline is also visible as a small shift in electrical conductivity and in the oxygen profiles as a typical peak due to the accumulation of photosynthetic algae in this zone of increasing water density.

- (3) The layer between about 20 and 60 m depth, which we will refer to as the hypolimnion. It is a seasonally mixed layer, the temperature of which is almost constant in time and space and close to the temperature of maximum density of water under in-situ conditions (about 3.9 °C).
- (4) The chemocline, a layer between about 60 and 70 m depth characterized by a strong increase of electrical conductivity, indicating a change in the chemical composition of the water. In the chemocline, the temperature increases from about 4 to 5 °C. The chemocline is also very prominent in the oxygen profile, as a change from oxic to anoxic conditions within a few meters. This characteristic transition in redox conditions is sharper than the transition in conductivity and temperature, as it occurs in the uppermost part of the chemocline.
- (5) The monimolimnion below about 70 m depth, which never takes part in the seasonal circulation of the mixolimnion. The monimolimnion is less uniform than the epilimnion and hypolimnion. Temperature and conductivity increase throughout the monimolimnion, although much less than in the chemocline. The monimolimnion is moderately mineralized (conductivity around 400 $\mu\text{S cm}^{-1}$) and completely anoxic.

Layers 1 to 3 form the so-called mixolimnion, because each spring and fall, when the temperature of

Figure 2. Bathymetric map of Lac Pavin (digitized from Delebecque, 1898). Depth contours are labeled in meters. Positions where CTD profiles were taken on 10 and 11 September 1996 are indicated with numbers, in chronological order (missing numbers are due to calibration measurements). All water samples were taken at the central station 4.

the epilimnion reaches 4 °C, the thermocline vanishes and the waters of these layers are mixed. As a result, the electrical conductivity is almost constant in the entire mixolimnion at a value of about $50 \mu\text{S cm}^{-1}$, corresponding to fresh, low-mineralized surface water.

The temperature of the monimolimnion remained practically unchanged between 1994 and 1996. Indeed, below 75 m depth the two profiles are identical within measurement precision. This finding suggests that the monimolimnion is at steady state with respect to the geothermal heat flow. The conductivity was also quite similar in both years throughout the profile, except near the top of the chemocline, where the gradients of temperature and conductivity were weaker in 1996 than in 1994. Oxygen in the mixolimnion was somewhat lower in 1996, and the oxic/anoxic interface had risen by about 5 m compared to 1994. Both

the rise of the transition to anoxic conditions and the broadening of the chemocline may be attributed to a less effective and deep-reaching mixing in the spring of 1996 as compared to 1994.

A very interesting feature of the 1996 profile are the temperature fluctuations between 40 and 50 m depth (Fig. 1a, insert). They resemble the signature of an intrusion of water, possibly from a sublacustrine spring at this depth. No similar feature is present in the conductivity data, whereas some small fluctuations can be seen in the oxygen profile at the same depth. A series of CTD profiles spread over the entire lake was recorded in 1996 to confirm this observation and map its horizontal extent. The location of the sampling stations are indicated in the bathymetric map of Lac Pavin (Fig. 2).

Figure 3. Comparison of three representative temperature profiles from stations in the northeast (23), center (4), and south (13) of the lake, in the depth range between 35 and 57 m. The profiles from the northeast and center show signs of an intrusion of cold water at about 45 m depth.

The temperature anomaly was found only in profiles taken in the northeastern sector of the lake. Therefore, this region was more densely sampled. The signal becomes apparent if profiles from the northeast are compared to those from the remainder of the lake (Fig. 3). Profile 13, just south of the center of the lake, shows some small temperature fluctuations between 40 and 55 m depth, but no major anomaly. In the northeast, as exemplified by profile 23 in Figure 3, there is a clear signal of an intrusion of cold water at around 47 m depth. Whereas the intrusion is confined to a layer of a few meters width in some of the northeastern profiles, it spreads over almost 10 m depth at the center of the lake (profile 4 in Fig. 3). The temperature signal of about 0.06°C may appear small, but it is highly significant compared to the resolution of the instrument (0.001°C). However, it could hardly have been detected in earlier temperature data with lower resolution. Furthermore, the signal may be missed in data from the center of the lake, such as our profile from 1994, because it appears to originate from the northeast.

To visualize the extent of the temperature anomaly, a horizontal section at 47 m depth and a vertical E–W cross-section between 40 and 54 m depth are shown in Figure 4. The horizontal section clearly shows a cold water tongue reaching from the NE shore towards the center of the lake, with a length of about

400 m and a width of about 250 m. Since the vertical section is not oriented along this tongue, but strictly in E–W direction, only a lens is visible in this graph. Near the lake center, the almost closed 4.1°C isotherm and the depression of the 4.3°C isotherm indicate a vertical extent of the lens of at least 6 m. The tongue is also characterized by slightly lower oxygen concentrations and higher light transmissivity, though these signals are less clear than the temperature anomaly (Schmid, 1997). No anomaly of electrical conductivity was found. The data strongly hint towards the existence of a sublacustrine spring at a depth between 40 and 50 m. This spring appears to discharge cold, clear, and oxygen depleted water, with a low mineralization comparable to local surface water. The finding of a fresh water spring in the mixolimnion is in strong contrast to the previous hypothesis of an input of warm, highly mineralized water to the monimolimnion (Martin, 1985).

3.2. Tritium and CFCs

The radioactive hydrogen isotope tritium (^3H) decays with a half-life of 12.38 years (Oliver et al., 1987) to the stable ^3He . Tritium concentrations in precipitation exhibited a sharp peak in 1963 as a result of thermonuclear weapons tests in the atmosphere, conducted in the 1950s and early 1960s. The peak of tritium concentrations in precipitation provides an ex-

Figure 4. Cross-sections of the temperature distribution. Upper panel: horizontal section at 47 m depth. Points indicate the locations of CTD profiles (compare Fig. 2). Lower panel: Vertical E–W section through the lake center (along the dashed line in the upper panel) between 40 and 54 m depth. Both sections show signs of an intrusion of cold water from the NE shore.

cellent hydrological tool to track the fate of meteoric water. Several investigators applied this tool to Lac Pavin to study its water balance and deep water exchange rate (Meybeck et al., 1975; Martin, 1985; Camus et al., 1993). However, the interpretation of tritium data is complicated by the uncertainty about the presence, size, and tritium content of a hypothetical sublacustrine spring.

The chlorofluorocarbons (CFCs) are anthropogenic compounds that have entered surface waters via

gas exchange with the atmosphere in steadily increasing concentrations over the past six decades. Only recently, this increase has been stopped due to the ban on CFC production in order to protect the ozone layer (Montzka et al., 1996). CFCs constitute an additional environmental tracer to investigate the origin and residence time of water. Besides applications in the ocean and in groundwaters, CFCs have also been used to track deep water renewal in lakes (e.g., Weiss et al., 1991; Peeters et al., 1997a, 2000).

Table 1. Tritium data

Depth (m)	³ H (TU)
<i>7 August 1993</i>	
30	15.9 ± 1.3
70	12.5 ± 0.4
<i>12 September 1996</i>	
5	13.4 ± 0.7
20	12.8 ± 0.6
30	11.8 ± 0.3
40	11.5 ± 0.5
50	14.9 ± 0.8
60	11.1 ± 0.6
65	11.2 ± 0.8
70	7.2 ± 0.8
75	3.6 ± 1.3
80	4.8 ± 0.7
90	4.0 ± 0.5

Tritium concentrations in Lac Pavin reflect the division of the water column in mixo- and monimolimnion (Table 1, Fig. 5a). In 1996, the tritium concentrations in the monimolimnion were about 4 TU (tritium units, 1 TU corresponds to a ³H/H ratio of 10⁻¹⁸), clearly lower than in the mixolimnion (≈12 TU) and in contemporary precipitation (≈ 18 TU at Thonon-les-Bains in 1995, IAEA/WMO, 2001). Such a difference of tritium concentrations has been observed in all previous tritium profiles from the lake (Alvinerie et al., 1966; Camus et al., 1993; Martin, 1985; Meybeck et al., 1975). Besides the major change at the chemocline, there is only a slight decrease of tritium with depth in the mixolimnion, whereas the tritium concentrations in the monimolimnion appear to be more or less uniform. The high tritium concentration of the 50-m sample does not fit in the overall pattern. Interestingly, this anomaly occurs at the same depth as the temperature anomaly discussed above. Unfortunately, only tritium data from 1993 and 1996 are available, as the 1994 profile was lost due to experimental problems.

The CFC concentrations also exhibit a sharp drop at the chemocline (Table 2, Fig. 5b,c). Concentrations in the hypolimnion were approximately constant at a few pmol kg⁻¹. Below 70 m the concentrations were below the detection limit (<0.02 pmol kg⁻¹), except for the 1994 CFC-11 data. Apparently, some mechanism removes any CFCs that are transported across the

Table 2. CFC data

Depth (m)	CFC-12 (pmol kg ⁻¹)	CFC-12 age (year)	CFC-11 ^a (pmol kg ⁻¹)	CFC-11 age (year)
<i>20 September 1994</i>				
2	2.11	2.5	3.41	9.1
15	3.17	2.4	5.61	8.3
30	3.01	5.7	5.79	8.7
40	3.02	5.7	5.50	9.8
50	3.24	2.9	5.69	9.0
60	2.70	7.9	4.98	11.5
65	1.06	22.4	0.67	30.7
70	0.44	29.7	0.31	36.0
80	<0.02	>48	0.12	40.3
85	<0.02	>48	0.20	38.7
90	<0.02	>48	0.27	37.1
<i>12 September 1996</i>				
5	1.94	4.0	3.46	8.9
20	2.94	6.7	5.70	9.6
40	2.85	9.0	5.86	10.3
50	2.75	9.7	5.71	11.0
60	2.39	12.6	3.90	18.3
65	1.20	23.4	0.82	31.4
75	<0.02	>50	<0.01	>46
85	<0.02	>50	<0.01	>46

Analytical errors of the concentrations are about ±2% for all samples. Corresponding errors of the CFC ages are less than 1 year.

^aCFC samples from 1994 were stored for 2 years before analysis, which may have affected particularly the CFC-11 concentrations (see text).

chemocline, most likely the well-known anaerobic microbial CFC degradation (e.g., Khalil & Rasmussen, 1989; Lovley & Woodward, 1992; Oster et al., 1996). Despite the long storage of the 1994 samples, the CFC profiles from 1994 and 1996 look very similar even for CFC-11, for which degradation in the copper tubes had to be expected (Hofer & Imboden, 1998). Surprisingly, a small amount of CFC-11 was detected in the 1994 samples from the monimolimnion. We consider the 1994 CFC-11 results to be less reliable due to the possibility of storage-related artefacts and hence do not use them any further.

The difference of CFC concentrations between the epilimnion and the hypolimnion is mainly a temperature effect. Since the solubilities of both CFC-12 and CFC-11 decrease strongly with increasing temperature (Warner & Weiss, 1985), the relatively warm surface water in September contains less CFCs than the cold hypolimnion. Interestingly, the CFC-12 result from

Figure 5. Transient tracer profiles from samples taken near the center of Lac Pavin on 7 August 1993, 20 September 1994, and 12 September 1996. (a) Tritium. 1 TU (tritium unit) corresponds to a $^3\text{H}/\text{H}$ ratio of 10^{-18} . Samples for 1994 were lost due to experimental problems. (b) CFC-12. (c) CFC-11. 1994 samples were stored for 2 years prior to analysis and may be affected by chemical reactions in the copper tubes. (d) Calculated apparent CFC ages. Estimated errors of ± 1 year are shown for the CFC-12 ages. CFC-11 ages are upper limits only, because of the possibility of degradation, particularly for the 1994 samples.

50 m depth in 1994 appears anomalously high, which would indicate addition of colder or more recent water at this depth, possibly by a sublacustrine spring. We can only speculate whether this anomaly is real and related to the tritium and temperature anomalies observed in 1996 at the same depth.

The CFC concentrations in the mixolimnion can be interpreted in terms of the water residence time with respect to gas exchange at the surface. From the observed CFC concentrations and the water temperature, the atmospheric partial pressure of CFCs that would be in equilibrium with the CFCs dissolved in the water can be calculated. This partial pressure can then be compared with the historical increase of CFC partial pressures in the atmosphere (e.g., Busenberg et al., 1993). Assuming that the water had once been in equilibrium with the atmosphere, this comparison yields the time of the last contact of the water with the atmosphere. The apparent CFC water age is defined as the difference between that time and the time of sampling.

CFC-11 water ages appear unrealistically high and constant with depth in the mixolimnion. As CFC-11 may be affected by anoxic degradation, either within the lake or in the copper tubes between sampling and analysis, we only discuss the CFC-12 results in the following. CFC-12 water ages increase from about 3 years in the epilimnion to about 10 years in the deep hypolimnion (Table 2, Fig. 5d). In the chemocline they rise dramatically, and in the monimolimnion

the apparent water age is larger than 50 years, since no CFC-12 is detectable. However, because of the possibility of anoxic degradation even of CFC-12 in this layer, the absence of CFC-12 cannot simply be interpreted in terms of water ages.

The exchange between the CFC- and O_2 -depleted monimolimnion and the oxic mixolimnion is likely to be small. Hence, in the mixolimnion, the CFC-12 ages should give a rough estimate of the water residence time with respect to gas exchange at the surface, i.e., of the intensity of the vertical mixing. It is astonishing that the ages are significantly different from zero in the shallow and well mixed epilimnion. This could be due to a time lag in the equilibration of the surface water with the rising concentrations in the atmosphere, as is typically observed in the ocean or large lakes (Weiss et al., 1991). However, in a small lake with a shallow epilimnion this explanation appears unlikely. The non-zero water ages may be the result of slow CFC equilibration during a period of cooling of the surface water in fall.

The CFC-12 water age below 30 m depth is significantly larger than in the epilimnion. It appears that the exchange of water between the deeper part of the mixolimnion and the epilimnion takes several years. In lakes which mix regularly every winter, one would expect apparent tracer water ages to be less than a year (e.g., Torgersen et al., 1977; Imboden et al., 1981; Aeschbach-Hertig et al., 1996a). The larger apparent residence times in Lac Pavin are thus an indication

that the seasonal mixing may be less efficient than expected.

3.3. Helium and CO₂

The data on He isotopes, the carbonate system, and other gases have been discussed and interpreted in terms of He and CO₂ fluxes into the lake in the framework of a simple box model by Aeschbach-Hertig et al. (1999a). In the present study, the He data are used together with transient tracer data as a constraint for a detailed model of the physical processes in Lac Pavin, which yields refined estimates of the He and CO₂ fluxes.

As most dissolved substances, the He concentrations reflect the vertically layered structure of Lac Pavin. He concentrations are near equilibrium with the atmosphere only in the epilimnion. In the hypolimnion, they are higher by up to a factor of 3, in the monimolimnion by up to a factor of 70 (Aeschbach-Hertig et al., 1999a). The large He excess in the monimolimnion clearly indicates a subsurface input of He. The origin of this He can be derived from the ³He/⁴He ratio, which increases from values close to the atmospheric ratio R_a (1.384×10^{-6} , Clarke et al., 1976) in the epilimnion to values close to 9×10^{-6} ($6.5 R_a$) in the monimolimnion. From the almost perfect correlation between the concentrations of ³He and ⁴He in Lac Pavin ($R = 0.99998$), the isotope ratio of the excess He component is determined to be $(9.09 \pm 0.01) \times 10^{-6} = (6.57 \pm 0.01) R_a$ (Aeschbach-Hertig et al., 1999a). This high ³He/⁴He ratio clearly indicates a mantle source of the excess He. The isotopic ratio of this source is indistinguishable from ratios measured in fluid inclusions in xenoliths from the Massif Central ($6.53 \pm 0.25 R_a$) (Dunai & Baur, 1995). Thus, we interpret the He in Lac Pavin as derived from the regional sub-continental mantle reservoir.

Usually, the combination of tritium and ³He concentrations in lakes provides a powerful tool to quantify the water residence time in terms of ³H–³He water ages (Torgersen et al., 1977; Kipfer et al., 2002). However, in Lac Pavin, tritiogenic ³He is negligible compared to mantle ³He and cannot be used to calculate ³H–³He water ages. The same problem has been encountered in other lakes affected by an input of mantle He (Kipfer et al., 1994; Aeschbach-Hertig et al., 1996b; Clark & Hudson, 2001).

All carbonate species, in particular dissolved CO₂ (given as $H_2CO_3^* = CO_2(aq.) + H_2CO_3$) and total CO₂ (ΣCO_2), can be calculated from pH and alkalinity,

Table 3. The carbonate system

Depth (m)	<i>T</i> (°C)	pH (–)	Alkalinity (mmol l ^{–1})	H ₂ CO ₃ [*] (mmol l ^{–1})	ΣCO ₂ (mmol l ^{–1})
<i>12 September 1996</i>					
5	14.48	8.30	0.453	0.0054	0.454
20	4.78	7.49	0.440	0.043	0.483
30	3.97	7.11	0.429	0.104	0.533
40	3.98	6.84	0.447	0.212	0.659
50	4.00	6.57	0.448	0.396	0.844
60	4.21	6.18	0.587	1.25	1.83
65	4.48	5.96	1.78	6.21	7.99
70	4.74	5.92	3.35	12.5	15.8
75	4.89	5.91	3.85	14.6	18.5
80	4.97	5.91	4.20	15.9	20.1
85	5.01	5.91	4.46	16.9	21.4
90	5.04	5.91	4.35	16.5	20.9
Error ^a ± 0.01 ± 0.1 ± 2% ± 20% ≤ ± 20%					

^aErrors for *T*, pH, and alkalinity are estimated measurement uncertainties. The 20% error of the calculated H₂CO₃^{*} follows from the error of pH, and the error of ΣCO₂ can be calculated by error propagation for the sum of alkalinity and H₂CO₃^{*}.

which were measured in September 1996 (Table 3). The calculated value of H₂CO₃^{*} depends strongly on pH and is therefore accurate only within ± 20%. Our alkalinity and pH data agree with the results of Michard et al. (1994) from 1992 within analytical uncertainty.

4. Discussion

To obtain a comprehensive understanding of the physical dynamics of Lac Pavin, we developed a numerical lake model, using the modeling tool AQUASIM (Reichert, 1994). This flexible software for the modeling of aquatic systems offers a lake compartment for the definition of a one-dimensional vertical advection-diffusion model. It also incorporates powerful methods to perform parameter estimations by inverse modeling.

The model was set up to simulate the temporal evolution of the vertical distributions of tritium, ⁴He, ³He, CFC-11, and CFC-12, and to derive the relevant physical parameters controlling their concentrations by inverse modeling. However, since ³He and ⁴He are strictly correlated (Aeschbach-Hertig et al., 1999a), and because of the uncertainties related to the CFC-11 data, only tritium, ⁴He (≈ total He), and CFC-12 were used as fit targets for the parameter estimation. Model

runs started in 1940, when significant input of anthropogenic CFCs and tritium began. Target values for the modeled concentrations were our measured data from the years 1993–1996, plus earlier tritium data Alvinerie et al., 1966; Meybeck et al., 1975; Camus et al., 1993). Although the number of observed data points is large (91), the number of really independent observations is much smaller, because for instance tritium concentrations in the mixolimnion are practically constant with depth. Hence, it is important to keep the number of free model parameters small in order to obtain meaningful results from the inverse modeling. Thus, as many parameters as possible were set based on prior knowledge.

Since the choice of preset and free parameters is not unique, we developed several scenarios with different choices of parameter sets and explored their ability to model the observed data. The agreement between the model scenarios and the data can be quantified in terms of χ^2 , the sum of the weighted squared deviations between the modeled and measured concentrations:

$$\chi^2 = \sum_i \frac{(C_i - C_i^{\text{mod}})^2}{\sigma_i^2}, \quad (1)$$

where C_i^{mod} are the modeled concentrations of ^4He , ^3H , and CFC-12, C_i are the measured concentrations, and σ_i their experimental 1σ -errors. Optimal parameter values are those which minimize χ^2 . With 91 data points and five to eight free parameters we have typically about 85 degrees of freedom. For a perfect agreement of the model and the data within their uncertainties one would expect χ^2 to be close to the number of degrees of freedom. However, for a model of a complex natural system such as Lac Pavin with only a few fit parameters such a perfect agreement is not to be expected. For instance, the model does not include interannual variations of climatic parameters such as surface temperature, ice cover, and wind speed which influence gas exchange as well as mixing depth and intensity, and is therefore a priori incapable to reproduce the respective interannual variation present in the data. Therefore, a formal χ^2 test was not applied. Nevertheless, it is possible to distinguish between different scenarios, when the χ^2 values obtained from best fits of the respective scenarios differ strongly. Furthermore, the inversion by least squares fitting allows to estimate confidence limits for the derived values of the parameters.

Table 4. Bathymetric data

Depth (m)	Area (km ²)	Volume (10 ⁶ m ³)
0	0.445	24.1
10	0.414	19.8
20	0.371	15.9
30	0.333	12.4
40	0.289	9.24
50	0.242	6.58
60	0.200	4.38
70	0.164	2.56
80	0.132	1.08
90	0.057	0.065

Data were obtained by digitizing the bathymetric map of Delebecque (1898).

A general boundary condition for the lake model is the lake bathymetry. Because for the 1-D vertical model a more detailed bathymetry was needed than available from the box-models in the literature, we digitized the bathymetric map of Delebecque (1898) and calculated cross-sectional areas of the lake at intervals of 10 m depth. A cubic spline interpolation of these data yielded depth dependent values of volume and cross section (Table 4). The horizontal layers of the model are 1 m thick, in order to be able to resolve sharp concentration gradients.

In the following subsections, we discuss the main physical aspects of the system and their representation in the model. We particularly focus on the parameters that are needed in the model to describe the relevant physical processes. We discuss which parameters can be reasonably well estimated from independent observational data and which have to be treated as free parameters. For the latter, the results of the inverse modeling are presented.

Since the water balance of Lac Pavin is a controversial issue, the different hypotheses about water inputs (Section 4.1) were implemented as model scenarios (Table 5). Major questions concern the existence, location, discharge, and transient tracer concentration of sublacustrine springs. The last issue is related to the problem of reconstructing the input history of tritium (Section 4.2). A fundamental quantity in our model is the vertical turbulent diffusivity $K(z)$, the parameterization of which is based on an analysis of the density stratification and stability of the water column (Sections 4.3 and 4.4). Further parameters that were needed in the model or could be determined by

Table 5. Model parameters in different scenarios

Parameter (unit)		Scenario					
		Martin	Camus	Meybeck	young	old	standard
Q_p	(l s ⁻¹)	19	18	18	18	18	18
Q_r	(l s ⁻¹)	34	5	40	20	20	20
Q_{45}	(l s ⁻¹)	–	–	–	6	15	20
Q_{85}	(l s ⁻¹)	40	35	–	–	–	–
a_{Tr}	(–)	0.71	1	0.51	0.49	0.71	0.5
$C_{Tr,45}$	(TU)	–	–	–	$C_{Tr,p}$	0	$C_{Tr,p}$
$C_{F,45}$	(pmol kg ⁻¹)	–	–	–	$C_{F,eq}$	0	$C_{F,eq}$
$C_{He,85}$	(cm ³ STP g ⁻¹)	2.1	2.1	–	–	–	–
K_{thermo}	(m ² s ⁻¹)	9×10^{-5}	1×10^{-3}	5×10^{-6}	5×10^{-6}	3×10^{-6}	5×10^{-6}
K_{hypo}	(m ² s ⁻¹)	2×10^{-3}	2×10^{-4}	9×10^{-6}	1×10^{-5}	9×10^{-6}	9×10^{-6}
K_{chemo}	(m ² s ⁻¹)	6×10^{-8}	8×10^{-8}	4.9×10^{-8}	5.2×10^{-8}	5.0×10^{-8}	5.2×10^{-8}
K_{moni}	(m ² s ⁻¹)	3×10^{-5}	1×10^{-4}	6×10^{-7}	6×10^{-7}	6×10^{-7}	6×10^{-7}
F_{He}	(cm ³ STP m ⁻² s ⁻¹)	–	–	2.2×10^{-8}	2.3×10^{-8}	2.2×10^{-8}	2.3×10^{-8}
χ^2	(–)	22 000	17 000	462	400	467	406

Optimized values of free model parameters are given in italics. Other parameters were preset based on the respective literature sources (Meybeck et al., 1975; Martin, 1985; Camus et al., 1993) or on our own estimates (scenarios ‘young’, ‘old’, and ‘standard’).

Description of parameters:

Q , Water input fluxes from direct precipitation (Q_p), catchment runoff (Q_r), and sublacustrine springs centered at depths of 45 m (Q_{45}) and 85 m (Q_{85}), respectively.

a_{Tr} , Factor to scale the tritium input record from Thonon to local conditions.

C , Concentrations of tritium (Tr), CFCs (F), and helium (He) in the respective input fluxes. $C_{Tr,p}$ is given by $a_{Tr} \cdot C_{Tr}$ (Thonon). Solubility equilibrium concentrations are calculated according to Warner & Weiss (1985) for CFCs ($C_{F,eq}$), and Weiss (1971) for He ($C_{He,eq}$).

K , Vertical turbulent diffusivity in the layers epilimnion (epi), thermocline (thermo), hypolimnion (hypo), chemocline (chemo), and monimolimnion (moni).

F_{He} , Uniform flux of He from the sediment.

τ_{mix} , Duration of seasonal mixing period in spring. Duration of fall mixing is $\tau_{mix}/2$.

d_{mix} , Depth of complete seasonal mixing ($K = K_{epi}$ above that depth during mixing intervals).

The following model parameters were preset in all scenarios:

$C_{Tr,r} = C_{Tr,p}$; $C_{F,r} = C_{F,p} = C_{F,eq}(T_{surface})$; $C_{He,r} = C_{He,p} = C_{He,eq}(T_{surface})$; $C_{He,45} = C_{He,eq}(4^\circ C)$;

$K_{epi} = 10^{-2} \text{ m}^2 \text{ s}^{-1}$; Duration of ice cover = 2 months.

The following model parameters were usually preset, but separately optimized as additional parameters in the standard scenario:

$\tau_{mix} = 20$ days (duration of seasonal mixing period). Optimized: 7 days.

$d_{mix} = 30$ m (depth of seasonal mixed layer). Optimized: 25 m.

$v_{g,600} \approx 0.55 \text{ m day}^{-1}$ (gas exchange velocity at $Sc = 600$). Optimized: 0.32 m day^{-1} .

$k_{F12} = 0.1 \text{ pmol kg}^{-1} \text{ year}^{-1}$ (CFC-12 degradation rate). Optimized: $0.07 \text{ pmol kg}^{-1} \text{ year}^{-1}$.

$k_{F11} = 1 \text{ pmol kg}^{-1} \text{ year}^{-1}$ (CFC-11 degradation rate). Optimized: $0.7 \text{ pmol kg}^{-1} \text{ year}^{-1}$.

inverse modeling are the duration and depth of the seasonal mixing (Section 4.5), the gas exchange at the surface (Section 4.6), the flux of mantle He (Section 4.7), and the rates of CFC degradation in the anoxic monimolimnion (Section 4.8).

4.1. Water balance

This point is usually trivial in lake models, but in the case of Lac Pavin it is one of the most controversial

issues, which severely complicates the modeling task. The most obvious way to constrain the water balance would be to measure the lake’s outflow. Unfortunately, only few direct measurements of the outflow have been made (Meybeck et al., 1975; Poulin, pers. comm.). Another approach is to estimate the input from the total precipitation on the catchment area. From the digitized map we obtain a value of 445 000 m² for the surface area of the lake, and the area of the surround-

ing crater rim has been estimated to about 200 000 m² (Poulin, pers. comm.). However, there is a subaerial spring on the southeastern shore which may be fed by water from outside the crater itself, and which yields 10 l s⁻¹ according to Meybeck et al. (1975). These authors estimated the total catchment area to be 1 200 000 m², whereas Poulin (pers. comm.) even considered a total catchment area of 1 800 000 m².

According to Meybeck et al. (1975) the total water input by direct rain, runoff from the catchment, and the subaerial spring is at most 58 l s⁻¹. Since the four measured values of the outflow were all larger than this, the existence of sublacustrine springs was suggested. Martin (1985) quantified this input by using a two-box model of the lake (moni- and mixolimnion) to reconstruct the historical development of tritium concentrations in the lake. The resulting inputs were 53 l s⁻¹ of meteoric water at the lake surface and 40 l s⁻¹ of tritium free water at the lake bottom. Camus et al. (1993) reassessed this model based on new tritium data from 1987, and came up with inputs of 23 l s⁻¹ at the surface and 35 l s⁻¹ at the bottom.

We reassessed the meteoric water input based on the estimates of Meybeck et al. (1975) for the mean precipitation (40 l s⁻¹ km⁻² = 1.26 m year⁻¹) and for the total catchment area (1.2 km²), but assuming that 1/3 of the precipitation on the catchment is lost by evapotranspiration. We calculate inputs of 18 l s⁻¹ by direct precipitation on the lake (Q_p), and 20 l s⁻¹ by runoff from the catchment (Q_r). Martin (1985) used a very similar estimate for Q_p (19 l s⁻¹). The estimate of Q_r is less reliable because of the uncertainties about the size of the catchment area and the loss by evapotranspiration.

In the older literature (Martin, 1985; Camus et al., 1993) a large spring in the monimolimnion was postulated (40 l s⁻¹ and 35 l s⁻¹, respectively). However, recent research has shown that this hypothesis is not necessary to explain the tritium data and is clearly inconsistent with observations of geochemical parameters (Schmid, 1997; Viollier et al., 1997; Aeschbach-Hertig et al., 1999a). Schmid (1997) assumed no input to the monimolimnion but a spring discharge of 10 l s⁻¹ in the mixolimnion. In our model, two different sites of sublacustrine water input were assumed: Q_{45} is a spring discharging between 40 and 50 m depth (as suggested by the CTD data), whereas Q_{85} is located between 80 and 90 m depth.

Water output is accomplished by the Couze river (Q_{out}) and evaporation (Q_e). Q_e is calculated from the following seasonally varying parameters: the lake

surface temperature and wind speed (data from M. Poulin, pers. comm.), the temperature difference between water and air (estimated according to Krause, 1980), and the relative humidity (estimated according to Kuhn, 1977). The annual mean value of Q_e is about 7 l s⁻¹, corresponding to an evaporation of 0.5 m year⁻¹ from the lake surface. A similar estimate (6 l s⁻¹) was obtained by Martin (1985). Thus, the only well-constrained terms in our water balance for Lac Pavin are the fluxes at the lake surface by direct precipitation and evaporation, resulting in a net water input of $Q_s = Q_p - Q_e = 11 \text{ l s}^{-1}$. Output by the Couze river equals the sum of all inputs: $Q_{out} = Q_s + Q_r + Q_{45} + Q_{85}$.

The controversial assumptions about the water balance of Lac Pavin have profound effects on the model. We first have to discuss the issue of sublacustrine springs before we can reach conclusions about other parameters such as vertical diffusivity or He flux. Therefore, we implemented and compared a number of alternative scenarios for the water input by precipitation, runoff, and springs, which correspond to the different literature values and our new estimates. The assumptions and free parameters for the scenarios are listed in Table 5.

The scenarios 'Martin' and 'Camus' (corresponding to the two-box models of Martin, 1985, and Camus et al., 1993) with a large spring in the monimolimnion yield rather bad fits to the observed tracer data. The optimum values of χ^2 are in the range of 20 000 (Table 5). To illustrate the misfit, the results of the 'Camus' scenario for the tracer profiles in 1994 and 1996 are compared with the observed data in Figure 6. This scenario (as well as the 'Martin' scenario) underestimates the He and tritium concentrations in the monimolimnion (Fig. 6a-c) as well as the CFC-12 concentrations in the hypolimnion (Fig. 6d). These deviations are due to the conflicting constraints imposed by He and tritium on the diffusivity in the chemocline. A large diffusivity is the only way to bring tritium into the monimolimnion, which is constantly flushed with tritium-free water from the spring. However, a weak diffusive exchange is required to model the strong He gradient in the chemocline.

No satisfactory compromise between these constraints can be found, and the models with a large spring in the monimolimnion have to be rejected. Note that this result could not have been reached based on tritium only. The scenarios with a deep spring yield fairly good fits to the tritium data, if the turbulent diffusive exchange across the chemocline is increased

Figure 6. Comparison of modeled and observed tracer profiles. The results of a scenario with a deep spring ('Camus') are opposed to those from the 'standard' scenario with a spring in the mixolimnion. (a) Helium. Insert: Mixolimnion on enlarged scale. (b) Tritium data from 1987 (Camus et al., 1993) and 1996 (this study). (c) Tritium data from 1965 (Alvinerie et al., 1966), and 1970 (Meybeck et al., 1975). (d) CFC-12.

to allow sufficient diffusion of tritium into the monimolimnion. Indeed, the two-box models of Martin (1985) and Camus et al. (1993) postulate a significant exchange flux between the monimolimnion and the mixolimnion boxes. However, the corresponding high diffusivity in the chemocline is inconsistent with the He data.

In contrast, the scenario 'Meybeck' (according to Meybeck et al., 1975) without any sublacustrine spring yields a much better fit to the observed data ($\chi^2 = 462$, Table 5). Two scenarios with our estimate of the catchment runoff ($Q_r = 201 \text{ s}^{-1}$) plus a 'young' (recent tritium) or 'old' (tritium-free) spring in the mixolimnion yield similar χ^2 values (Table 5). Thus, the model enables us to rule out the existence of a significant spring in the monimolimnion, but not to unequivocally determine the exact size and distribution of water inputs to the mixolimnion.

4.2. Tracer input concentrations

Since the anthropogenic tracers tritium and CFCs are characterized by time dependent input histories over the past decades (Section 3.2), their concentrations in the inflowing water are essential boundary conditions for the model.

The historic development of CFC concentrations in the atmosphere has been reconstructed based on production data up to 1976 and direct measurements thereafter by several authors. As the differences between these histories are of the same order as the uncertainties due to experimental errors and temperat-

ure dependent solubilities, they are of little relevance for our purpose. In this study, the atmospheric CFC abundances were taken from Busenberg et al. (1993) for the years prior to 1977 and from the NOAA/CMDL Flask Program (Elkins et al., 1993; Montzka et al., 1996; data available at <http://www.cmdl.noaa.gov>) for later years. The corresponding equilibrium concentrations in the water were calculated according to Warner & Weiss (1985).

Tritium concentrations in precipitation have been monitored by a global network of measuring stations (IAEA/WMO, 2001). However, in order to determine the water budget based on observed tritium concentrations in the lake, it is essential to know the tritium concentrations in the local precipitation. Reliable local tritium input curves are quite difficult to obtain, despite the large number of monitoring stations in Europe. The reason is a substantial gradient of tritium concentrations in precipitation from low marine values at the Atlantic coast to higher values in the interior of the continent (continental effect). For instance, compared to the marine reference station Valentia (Ireland), the tritium concentrations at the French stations Le Mans and Thonon-les-Bains were found to be elevated by factors of 1.7 and 2.8, respectively (Weiss et al., 1979). The local precipitation at Lac Pavin can be expected to lie somewhere in between these values.

The problem of reconstructing the tritium input to Lac Pavin is further complicated by the uncertainty about the presence of a tritium-free spring. The effect of such a spring is similar to a reduction of the input concentrations. At least one free parameter has

to be used to scale tritium input records to the specific location and/or to account for the dilution by a sublacustrine spring.

Since the data series from Thonon is the longest, previous tritium models relied mainly on that record, extended by data from Ottawa for the period between 1953 and 1963. Meybeck et al. (1975) found from a linear regression of measurements in the Mont-Dore region against the data from Thonon that the local tritium concentrations were reduced by a factor of 0.71, which is in agreement with expectations. Martin (1985) probably used the same scaling, whereas Camus et al. (1993) apparently used the record from Thonon without any scaling to local conditions. Schmid (1997) constructed the local tritium input curve as a linear combination of the records from Valentia and Thonon. A combination which is approximately equivalent to a reduction of the Thonon data by a factor of 0.55 gave the best fit between measured and modeled tritium concentrations in Lac Pavin.

In this work, we construct a more detailed model of the tritium balance of Lac Pavin. Because our model resolves the seasonal variation of mixing, we incorporate the distinct seasonal variation of tritium input (e.g., Rozanski et al., 1991) by using monthly tritium data from IAEA/WMO (2001). In order to extend the record from Thonon, it was linked to the reference station Vienna according to procedures used in IAEA (1992), i.e., by a linear regression of the logarithms of the tritium concentrations. The record from Vienna, in turn, was extended with the earliest data from Ottawa. The extended monthly record for Thonon was then scaled to local conditions at Lac Pavin using a scale factor a_{Tr} , which was usually a free model parameter (Table 5). Note that a_{Tr} is not adjusted to fit the local precipitation measurements, but to yield a good fit to the tritium data from the lake. As an alternative, $a_{Tr} = 0.71$ was used, as suggested by Meybeck et al. (1975).

A further difference between our model and those of Martin (1985) and Camus et al. (1993) is that the tritium transfer between atmospheric water vapor and lake water was taken into account. The tritium flux due to condensation and evaporation can be described by the net evaporative water flux Q_e and an apparent concentration C_e (Imboden et al., 1977):

$$F_{Tr} = Q_e C_e = Q_e \frac{\alpha^* (h C_p - C_s)}{1 - h}, \quad (2)$$

where h is the normalized humidity (water vapor content of the air relative to saturation at the water temperature), $\alpha^* = 0.89$ describes the fractionation

of tritium during evaporation, and C_p and C_s are the tritium concentrations in precipitation and surface water, respectively. Similarly to Q_e , the value of h was calculated from the seasonal variation of the relative humidity and the temperature difference between water and air. The annual mean value of h is 0.66. Since Q_e (7 l s^{-1} on average) is much smaller than the total water flow through Lac Pavin ($> 58 \text{ l s}^{-1}$ according to Meybeck et al., 1975), the tritium flux according to Equation (2) is of relatively minor importance. It was largest (about $2Q_e C_p$) in the years of the bomb peak, when C_p was much larger than C_s .

The general assumption determining the input concentrations in our model is that all inflows to the mixolimnion (Q_p , Q_r , and Q_{45}) are recent meteoric water, i.e., in equilibrium with the time-dependent atmospheric conditions, whereas the spring in the monimolimnion (Q_{85}), if present, delivers old, deep circulating water free of tritium or CFCs but with a high He concentration. The latter assumption implies that the age of the deep groundwater is at least 50 years. Since the spring in the mixolimnion (Q_{45}) appears to deliver cold and low-mineralized water, it seems unlikely that its water is that old. Yet, it may well have a residence time of several years or even decades. Its tritium and CFC concentration would then lag behind that of the surface input, and the signal of the tritium peak would be significantly reduced due to dispersion and radioactive decay. In principle, the tracer concentrations in Q_{45} could be estimated from an appropriate groundwater model (e.g., Maloszewski & Zuber, 1982). However, this would introduce at least one new, badly constrained model parameter (the groundwater residence time). Therefore, we chose to investigate only two alternative scenarios, namely with groundwater residence times of zero (standard case) and larger than 50 years (zero concentrations of tritium and CFCs).

In summary, the tracer input concentrations C_i corresponding to the water input fluxes Q_i are constrained as follows (compare Table 5): (i) C_p , C_r : atmospheric equilibrium at the variable surface temperature for CFCs, and historic concentrations in precipitation from Thonon scaled by the factor a_{Tr} for tritium; (ii) C_{45} , atmospheric equilibrium at 4°C for CFCs and equal to C_p for tritium in the standard case, or zero for tritium and CFCs as an alternative (scenario 'old spring'); (iii) C_{85} , zero for both tritium and CFCs.

The results of the inverse modeling with respect to the tritium input scale parameter a_{Tr} reflect the uncertainty about the water balance of Lac Pavin. If it

is assumed that no tritium-free water enters the lake (scenarios ‘Meybeck’, ‘young spring’, Table 5), the scaling factor has to be about 0.5, i.e., the local tritium concentrations in precipitation would have to be about one half of the values measured at Thonon. If one insists on the tritium input curve as used by Meybeck et al. (1975), with $a_{Tr} = 0.71$, a substantial input of tritium-free water is needed to explain the low observed tritium contents of Lac Pavin. As discussed above, we can rule out such an input to the monimolimnion (scenarios ‘Martin’ and ‘Camus’), but it could be present in the mixolimnion (scenario ‘old spring’).

Obviously, tritium on its own cannot be used to unequivocally determine the water balance of Lac Pavin, because of the uncertainties related to its input. If the surface water (Q_p , Q_r) and the spring in the mixolimnion (Q_{45}) are assumed to have the same tritium contents, the relative size of these contributions cannot be determined. The best fits are obtained for a moderate combined freshwater input $Q_{in} = Q_p + Q_r + Q_{45}$. The optimum is achieved in the ‘young spring’ scenario, with $Q_{45} = (6 \pm 3) \text{ l s}^{-1}$ and $Q_{in} = 44 \text{ l s}^{-1}$. However, also the scenario ‘Meybeck’ with $Q_{45} = 0$ and $Q_{in} = 58 \text{ l s}^{-1}$ yields acceptable results. The spring in the mixolimnion can be separated from the surface water input only if it is assumed to deliver tritium- and CFC-free water, as in the scenario ‘old spring’. In that case, its size is constrained to $(15 \pm 1) \text{ l s}^{-1}$, but this result also depends on the assumptions for a_{Tr} and Q_r .

Combining the results from the modeling exercise with the evidence from the CTD profiles, we think that the most realistic scenario is one with no (or a very small) spring in the monimolimnion, a relatively small freshwater spring in the mixolimnion, and a moderate input by surface runoff. Since this conclusion is of a rather qualitative nature, we use it to construct a ‘standard’ model of Lac Pavin, in which the free parameters discussed so far are fixed at round numbers, to make clear that these are only estimates and should not be taken at face value. However, the structure of the model, with a spring in the mixolimnion rather than the monimolimnion, is a robust feature of our view of Lac Pavin. The parameters related to water and tritium input in the standard model are (Table 5): $Q_r = 20 \text{ l s}^{-1}$, $Q_{45} = 10 \text{ l s}^{-1}$, $Q_{85} = 0$, $C_{Tr,45} = C_{Tr,p}$, and $a_{Tr} = 0.5$. These parameters yield a fit to the observations which is hardly distinguishable from the optimum obtained with more free parameters. The standard model will be the basis of the following discussion of other model parameters.

4.3. Density stratification and stability

The peculiar temperature and conductivity profiles in Lac Pavin call for an analysis of the density stratification in terms of the stability of the water column. The water density is determined mainly by temperature and salinity. The relationship between conductivity, salinity, and density depends on the composition of the dissolved ions in the water. In Lac Pavin, the chemical compositions of the mixolimnion and the monimolimnion differ not only in terms of absolute concentrations, but also in terms of relative abundances of ionic species. For the derivation of polynomials that link conductivity to salinity and finally to density, the chemical analyses of Michard et al. (1994) and the methods outlined by Wüest et al. (1996) have been used.

The density is calculated in four steps. First, the measured electrical conductivity κ is normalized to a temperature of 20 °C:

$$\frac{\kappa}{\kappa_{20}} = a_0 + a_1 T + a_2 T^2. \quad (3)$$

Next, the normalized conductivity κ_{20} is related to the salinity S by an empirical polynomial relationship of the form:

$$\frac{S}{\kappa_{20}} = b_0 + b_1 \kappa_{20} + b_2 \kappa_{20}^2. \quad (4)$$

The density ρ is related to the salinity S by the coefficient of haline contraction β :

$$\beta = \frac{1}{\rho} \frac{\partial \rho}{\partial S}. \quad (5)$$

The value of β at 25 °C can be calculated from the partial molal volumes and the molar masses of the electrolytes dissolved in the lake water.

At last, the density $\rho(T, S)$ is calculated based on the equation of state of diluted seawater given by Chen & Millero (1986), but with a correction for the effect of the actual ion composition of the lake water. The correction is given by the ratio of the value of β calculated for the specific ion composition to the value calculated from the equation of Chen & Millero (1986) at 25 °C. All empirical parameters in Equations (3)–(5) depend on the specific ion composition of the water. The values derived for the mixo- and monimolimnion of Lac Pavin are given in Table 6 (Schmid, 1997). For the calculation of the density profiles the parameter values were switched at a depth of 60 m, which leads to a small discontinuity.

Table 6. Parameters for the calculation of normalized conductivity, salinity, and density

	a_0	a_1	a_2	b_0	b_1	b_2	β
Mixolimnion	0.601	0.0174	1.27×10^{-4}	8.45×10^{-4}	3.00×10^{-7}	-4.98×10^{-10}	0.778
Monimolimnion	0.608	0.0169	1.00×10^{-4}	8.29×10^{-4}	1.41×10^{-7}	-3.99×10^{-11}	0.784

Figure 7. Profiles of physical parameters calculated from the CTD profiles. (a) Water density (given as deviation from 1000 kg m^{-3}). (b) Stability N^2 (Equation (6)) on a logarithmic scale. (c) Contributions to N^2 from temperature (N_T^2) and salinity (N_S^2) gradients on a linear scale.

In the calculation of density from temperature, the warming due to adiabatic compression should be corrected by using the potential temperature rather than the *in situ* temperature (e.g., Peeters et al., 1996). However, the difference between potential and *in situ* temperature is negligible in Lac Pavin (about 0.001°C at the bottom). The density profiles from the 2 years look very similar (Fig. 7a). The major features are the density steps in the thermocline and the chemocline. The density gradient is very small in the hypolimnion (insert of Fig. 7a), but substantial in the monimolimnion.

For the analysis of the vertical stratification, it is convenient to examine the local stability or Brunt-Vaisälä frequency, which may be written as (Peeters et al., 1997b):

$$N^2 = -\frac{g d\rho}{\rho dz} = g \left(\alpha \frac{dT}{dz} - \beta \frac{dS}{dz} \right) \equiv N_T^2 + N_S^2, \quad (6)$$

where α is the coefficient of thermal expansion, the z coordinate is positive upwards and, again, the correction for the effect of adiabatic compression is neg-

lected. For a more general discussion of the stability in freshwater lakes see Imboden & Wüest (1995) or Peeters et al. (1996). The profiles of N^2 (smoothed by averaging the T and S gradients over 4-m depth intervals) and the two contributions to N^2 from temperature ($N_T^2 = g \cdot \alpha \cdot dT/dz$) and salinity ($N_S^2 = -g \cdot \beta \cdot dS/dz$) in Equation (6) are shown in Figures 7b,c.

The stratification of the upper 30 m of the water column is typical for temperate lakes. The stability is small in the mixed layer and very large in the thermocline due to the strong temperature gradient. It reaches a maximum of more than 10^{-3} s^{-2} at a depth of about 10 m. N_T^2 continues to dominate the stability down to about 25 m depth. At about 30 m depth, however, the temperature reached a minimum of 3.92°C in September 1994 and 3.96°C in September 1996 (insert of Fig. 1a). It is important to note that the temperature of maximum density (T_{md}) of water is about 3.98°C only at the lake surface, but decreases with increasing hydrostatic pressure by about 0.02°C per 10 m depth (Chen & Millero, 1986). Therefore, the temperature minimum in 1994 was very close to T_{md} , whereas at all other depths temperature remained clearly above

T_{md} (Fig. 1a). Hence, any increase of temperature with depth, as it occurs below 30 m depth, destabilizes the stratification of the water column.

Between 25 and 55 m depth, the temperature is so close to T_{md} that N_T^2 is very small (insert in Fig. 7c). The very slight temperature increase below the temperature minimum is therefore easily balanced by the steady small increase of salinity (see insert of Fig. 1b), resulting in a very weak stratification of this part of the water column ($N^2 \approx 10^{-7}$ to 10^{-6} s^{-2} , Fig. 7b). The positive gradients of temperature and salinity with depth are much larger in the chemocline between 60 and 70 m depth. N_S^2 by far overcompensates the negative value of N_T^2 (Fig. 7c). The resulting stability is large ($>10^{-4} \text{ s}^{-2}$), only one order of magnitude lower than in the thermocline. In the monimolimnion below 70 m depth, the gradients of temperature and salinity as well as the stability are somewhat smaller than in the chemocline, but far above the values in the mixolimnion. N^2 is larger than 10^{-5} s^{-2} due to the dominance of N_S^2 .

Since the entire water column below 30 m depth is unstable in temperature and stabilized by salinity only, enhanced mixing due to double diffusion could potentially occur. However, the fact that N_S^2 is everywhere much larger than $|N_T^2|$ appears to suppress this peculiar physical effect (Imboden & Wüest, 1995).

4.4. Vertical turbulent diffusion

A crucial parameter to describe transport in a 1-D vertical advection-diffusion model of a lake is obviously the profile of the vertical turbulent diffusivity $K(z)$. This quantity is related to the vertical density stratification. The action of wind and currents produces shear stress within the water column and provides the turbulent kinetic energy (TKE) to drive turbulent vertical mixing. In a stratified fluid, vertical mixing reduces the density gradient, which leads to an increase of the potential energy of the water column. Only a small fraction (on the order of 10%) of the TKE is converted into potential energy, whereas the majority is dissipated.

The stronger the stratification (N^2), the more energy is needed to create vertical turbulent mixing. Therefore, the vertical turbulent diffusivity K must be somehow inversely related to N^2 . The theoretical analysis of Welander (1968) showed that K and N^2 are related by:

$$K \propto (N^2)^{-q}, \quad (7)$$

with q somewhere between 1/2 and 1. Empirical tests of this relationship (e.g., Imboden et al., 1983; Imboden & Wüest, 1995) have shown that in some instances it provides reasonable fits to the $K(z)$ profile in the entire hypolimnion. Thus, although Equation (7) cannot yield reliable absolute values of K from N^2 , it may provide useful order of magnitude estimates. In particular, it may be used to estimate the shape of the $K(z)$ profile in the hypolimnion. With respect to Lac Pavin, the conclusion from the N^2 profiles of Figure 7b is that vertical turbulent mixing in the chemocline must be suppressed by about two orders of magnitude compared to the hypolimnion, and up to one order of magnitude compared to the monimolimnion.

To model the vertical profile of $K(z)$, we used two different approaches. Usually the water column was divided according to the stability profile into the five layers discussed in Section 3.1., each with a constant K value (K_{epi} , K_{thermo} , K_{hypo} , K_{chemo} , K_{moni}). Except for K_{epi} , these parameters were treated as free fit parameters. In the epilimnion, which by definition is a well-mixed layer, any K_{epi} value large enough to maintain homogeneous conditions yields a good fit to the constant concentrations. Thus, this parameter cannot be well constrained by inverse modeling. It is preferable to fix K_{epi} at an arbitrary, large value, which assures homogeneity in the epilimnion. We chose $K_{\text{epi}} = 10^{-2} \text{ m}^2 \text{ s}^{-1}$, because then the time-scale for turbulent mixing of the 10-m layer, $\tau = (10 \text{ m})^2 / 2K_{\text{epi}}$, is small (1.4 h).

In an alternative approach, Equation (7) with $q = 1$ was used to model the $K(z)$ profile below the thermocline. The average of the two measured N^2 profiles from 1994 and 1996 was used to define the shape of the $K(z)$ profile. The uppermost layers were modeled as in the standard case, with K_{epi} fixed at $10^{-2} \text{ m}^2 \text{ s}^{-1}$ and K_{thermo} as a free parameter. This approach reduces the total number of free parameters needed to define the $K(z)$ profile to two (a proportionality constant in Equation (7) and K_{thermo}).

Typical ranges for K in lakes are 10^{-6} to $10^{-5} \text{ m}^2 \text{ s}^{-1}$ in the thermocline and 10^{-5} to $10^{-4} \text{ m}^2 \text{ s}^{-1}$ in the hypolimnion (e.g., Li, 1973; Imboden et al., 1983). The scenarios with a large spring in the monimolimnion ('Martin' and 'Camus') yield optimum values for the respective parameters that are up to two orders of magnitude higher than the upper limit of these ranges (Table 5). In both scenarios, either K_{thermo} or K_{hypo} turns out to be on the order of $10^{-3} \text{ m}^2 \text{ s}^{-1}$ (Fig. 8a). These are clearly unrealistic solutions, as they imply that the mixolimnion of Lac Pavin is constantly mixed,

Figure 8. Profiles of the vertical turbulent diffusivity K during summer and winter stratification as estimated with different model scenarios (compare Table 5). (a) The standard scenario compared with scenarios with a spring in the monimolimnion. (b) Comparison of several scenarios without such a spring. The line labeled 'seasonal mixing' shows the $K(z)$ profile in the upper 30 m during seasonal mixing periods, as it was used in all scenarios. (c) The standard model compared with a scenario in which the shape of the $K(z)$ profile was estimated from the N^2 profile.

although a strong and persistent thermocline is always observed in summer.

The origin of the high diffusivities in these models is the large advective upward transport of dissolved substances from the monimolimnion into the mixolimnion implied by the postulated deep spring. These substances must somehow be removed from the mixolimnion to produce the sharp concentration gradients observed at the chemocline. For substances adsorbing to particles or forming insoluble compounds, it was hypothesized that this removal was accomplished by sedimentation, but Viollier et al. (1997) showed that the observed sedimentation fluxes are much too low. For gases such as He or CO₂, the removal could be accomplished by vertical mixing and gas exchange, but under realistic assumptions these processes are too slow to perform this task. Based on a box model, Aeschbach-Hertig et al. (1999a) already reached the conclusion that a large spring in the monimolimnion would imply permanent mixing of the mixolimnion to keep the He profiles at steady state.

The unrealistically high diffusivities and the bad fits to the observed data provide strong evidence against the scenarios with a spring in the monimolimnion. Hence, the scenarios 'Martin' and 'Camus' are rejected and not considered in the further discussion. In contrast, the standard model as well as all other scenarios without a spring in the monimolimnion yield a quite reasonable and well constrained $K(z)$

profile (Table 5, Fig. 8b). The plausibility of the $K(z)$ profile can be tested by comparison with the alternative approach for parameterization, in which K is assumed to be inversely proportional to N^2 . The two parameterizations of $K(z)$ yield quite similar results (Fig. 8c).

Of most interest for the transport of dissolved substances in Lac Pavin is the value of K_{chemo} , because the chemocline is the site of many distinct concentration gradients. According to Fick's law, the turbulent diffusive flux of any dissolved species across the chemocline equals the product of K_{chemo} and the concentration gradient. All scenarios yield values close to $5 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$ for K_{chemo} . In the alternative parameterization with K proportional to $1/N^2$, the minimum of K is $6.4 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$ in 64 m depth (resolution of 2 m). Note that these values are extremely low for lakes. They are only one order of magnitude larger than molecular diffusion coefficients for dissolved species, and a factor of two to three lower than the molecular diffusion of heat ($D_T = 1.35 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ at 4 °C). This implies that heat transport through the chemocline is actually accomplished by molecular rather than turbulent mechanisms. If this is the case, we can calculate the diffusive heat flow F_{th} through the chemocline from:

$$F_{\text{th}} = -D_T c \rho \frac{dT}{dz}, \quad (8)$$

where c is the heat capacity of water, and ρ is water density. Using the temperature difference between 60 and 70 m depth to estimate the mean temperature gradient in the chemocline in 1994 and 1996, heat flows of 40 and 30 mW m⁻² are derived, respectively. These results are in reasonable agreement with direct measurements of the heat flow from the sediment of Lac Pavin reported by Camus et al. (1993), which mostly lay between 21 and 28 mW m⁻². The data are consistent with the assumption of a steady state temperature in the monimolimnion, which implies that the heat flow through the chemocline must equal the geothermal heat flow.

The vertical turbulent diffusivity in the chemocline is directly related to the residence time of any conservative species in the monimolimnion, since it represents the only available transport mechanism. Strictly speaking, the water residence time in the monimolimnion is defined only in a box model by the ratio between the box volume and water flow. A way to estimate the water residence time in a continuous model as we describe it here, is to translate the diffusive flux through the chemocline into an advective exchange flux Q_{ex} by setting (Aeschbach-Hertig et al., 1999a):

$$Q_{\text{ex}} = K_{\text{chemo}} \frac{A_{\text{chemo}}}{d_{\text{chemo}}}, \quad (9)$$

where A_{chemo} and d_{chemo} are the cross-sectional area and the thickness of the chemocline, respectively. With $K_{\text{chemo}} = 5 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$, $A_{\text{chemo}} = 1.8 \times 10^5 \text{ m}^2$ (at 65 m depth), and $d_{\text{chemo}} = 10 \text{ m}$, Equation (9) yields $Q_{\text{ex}} = 0.9 \text{ l s}^{-1}$. This weak exchange flux corresponds to a water residence time $V_{\text{moni}}/Q_{\text{ex}}$ of 90 year in the monimolimnion (defined as the volume of $2.6 \times 10^6 \text{ m}^3$ below 70 m depth), with respect to exchange with the water of the mixolimnion.

An alternative approach to estimate water residence times is to simulate the evolution of an ideal age tracer in the model. In analogy to the properties of the real water age tracer given by the ³H–³He system, the ideal age tracer is defined by a unit source term in the water column (increase by one year per year) and a very large sink term at the surface. As a result, the ideal age is set to virtually zero in the epilimnion and measures the residence time in the deeper layers with respect to mixing with the surface layer. The quasi-steady state (constant except for seasonal variations in the mixolimnion) profile of this ideal age in Lac Pavin was calculated with the standard model. The resulting age profile is close to zero in the uppermost 10 m, and then increases approximately linearly to about 4

years at 60 m depth, which is in rough agreement with the CFC-12 ages (Fig. 5d). In the chemocline, the age increases rapidly to 86 years at 70 m depth, and then slowly to 96 years at the bottom of the lake. This result is in perfect agreement with the box-model estimate derived above.

4.5. Seasonal mixing

The division of Lac Pavin in five layers and the respective structure of $K(z)$ as discussed above is valid only for the periods with thermal stratification. This is certainly the case in summer, when the surface temperature is much larger than T_{md} . In winter, an inverse stratification develops, with surface temperatures smaller than T_{md} . For simplicity, the $K(z)$ -profile for the winter period was set equal to that in the summer stratification period, although the winter stratification is certainly weaker. The epilimnion is mixed with the hypolimnion to form the mixolimnion during each fall and spring overturn. According to Restituito (1987) as well as to regularly taken temperature profiles in the upper 40 m of the lake (Amblard, pers. comm.), the fall overturn takes place in December and is clearly weaker than the spring overturn, which starts in late March or early April.

In the model, the seasonal mixing is represented by a temporary increase of the vertical turbulent diffusivity in the mixolimnion to the high value chosen for the epilimnion. Two parameters were used to model the seasonal mixing: the duration of the mixing period in spring (τ_{mix}) and the depth of the mixed layer (d_{mix}). The weaker fall mixing was simulated by a shorter duration ($\tau_{\text{mix}}/2$) but the same mixing depth. It is difficult to simultaneously estimate the parameters of seasonal mixing and the profile of vertical diffusivity by inverse modeling, because of mutual correlations. Small values of the parameters describing the seasonal convective mixing can to some extent be compensated for by higher $K(z)$ -values. Since τ_{mix} and d_{mix} can be relatively well estimated from observational data, they were usually prescribed.

The historical data show that homothermal conditions with temperatures close to 4 °C at least in the uppermost 40 m of the water column last for about a month in spring. Thus, one could think that reasonable values for the parameters describing the seasonal mixing might be 1 month for τ_{mix} , and 60 m (entire mixolimnion) for d_{mix} . However, as pointed out by Van Senden et al. (1990), homogenization of only one parameter (e.g., temperature) does not necessarily im-

ply that complete mixing has occurred. Furthermore, it has to be taken into account that convective mixing is a complex, intermittent process, which can only roughly be approximated by a very high turbulent diffusivity in the model. The chosen value of K_{epi} of $10^{-2} \text{ m}^2 \text{ s}^{-1}$ assures rapid homogenization even for the entire mixolimnion (on a time-scale of $\tau = (60 \text{ m})^2 / 2K_{\text{epi}} = 2$ days). Such rapid transport over the full mixing period and depth may not be a realistic approximation of the actual mixing, which varies depending on surface cooling and wind energy input. Thus, τ_{mix} was set to 20 days only.

Closer inspection of the temperature profiles (Fig. 1a) shows that temperature is not completely homogeneous in the mixolimnion and that a characteristic minimum occurs at 30 m depth (Section 4.3). Since this temperature minimum is very close to the temperature of maximum density (T_{md}), it forms a barrier to convective sinking of water parcels due to cooling at the surface. It is interesting to note that in this respect the thermal structure of the small Lac Pavin is analogous to the huge Lake Baikal (Hohmann et al., 1997). The occurrence of the temperature minimum and the temperature increase in the lower mixolimnion suggest that complete homogenization during fall and spring mixing might reach only to a depth of 30 m. This assumption is also supported by the increase of the CFC-12 ages at about this depth (Fig. 5d). Hence, the mixing depth d_{mix} was set to 30 m.

In order to verify the choices made for τ_{mix} and d_{mix} , the standard scenario was run with either of the two as free parameters. Fitting τ_{mix} in addition to the $K(z)$ -profile shows that this parameter is very weakly constrained. The optimum is achieved at $\tau_{\text{mix}} = 7$ days, with an estimated uncertainty of ± 8 days. The reduction of τ_{mix} from the standard value of 20 d is compensated by an increased diffusive transport through the thermocline, by raising K_{thermo} from $5 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ to $7 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$. The fit is very slightly improved by this change (χ^2 is reduced from 406 to 397). The exact value of τ_{mix} thus seems quite unimportant for the model, and the choice of 20 days for the standard model does not significantly affect the results obtained for other parameters. In contrast, the model is more sensitive to changes of d_{mix} . The optimum for this parameter was found at $(25 \pm 4) \text{ m}$, with similar effects as from the change of τ_{mix} (K_{thermo} from $5 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ to $7 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$, χ^2 from 406 to 395). This result justifies the choice of $d_{\text{mix}} = 30 \text{ m}$, which is based on observational evidence. The

naïve choice of a mixing depth of 60 m would lead to a clearly worse fit to the measured data.

The general result of these investigations is that the prescribed mixing parameters are reasonable, although a somewhat weaker mixing (lower τ_{mix} and/or d_{mix}) would lead to slightly better fits. In contrast, much stronger, in particular deeper reaching, convective mixing can be excluded. High resolution CTD-measurements in all seasons would be needed to better constrain the actual development of convective mixing in time and space.

4.6. Gas exchange at the surface

The in- and output of the gaseous CFCs as well as the output of He from the lake is mainly accomplished by gas exchange at the lake surface. Therefore parameters such as surface water temperature, wind speed, and ice cover are important boundary conditions for the model, because they govern the gas exchange. Since gas solubilities, in particular those of the CFCs, are strongly temperature dependent, it is essential to include the seasonal variation of surface temperatures in the model. This variation was approximated with monthly mean surface temperature data measured in 1993 and 1994 by Poulin (pers. comm.). These data are in good agreement with historical temperature profiles (Pelletier, 1968; Ambard, pers. comm.).

The gas exchange velocity also depends on temperature, via the temperature dependence of the Schmidt number Sc (the ratio between kinematic viscosity of the water and the molecular diffusivity of the gas). Empirical relationships for $Sc(T)$ for several gases, including noble gases and CFCs, were reported by Wanninkhof (1992). The model parameter for gas exchange is $v_{g,600}$, the exchange velocity at $Sc = 600$, and depends on wind speed. Wanninkhof et al. (1990) and Upstill-Goddard et al. (1990) derived empirical relationships from experiments in lakes, which were confirmed by the results of Clark et al. (1995). Wind speed 10 m above the water surface of Lac Pavin was measured by Poulin (pers. comm.) in 1993 and 1994. Monthly average wind speed varied between 2.2 and 3.8 m s^{-1} , with a yearly mean of 2.7 m s^{-1} , for which the empirical relationships yield $v_{g,600}$ values of 0.55 m day^{-1} (Wanninkhof et al., 1990) and 0.80 m day^{-1} (Upstill-Goddard et al., 1990). In our model, gas exchange velocities for He and CFCs were calculated from the monthly mean data on wind speed and surface temperatures using the relationships of Wanninkhof et al. (1990) and Wanninkhof (1992). With

these assumptions, typical gas exchange velocities are 0.9 m day^{-1} for He and 0.3 m day^{-1} for CFCs.

In winter, usually an ice-cover develops on Lac Pavin, which interrupts the gas exchange. According to Alvinerie et al. (1966) and Meybeck et al. (1975) the ice cover can extend from late December until April in cold winters, whereas in mild winters no permanent ice cover forms. Thus, the model parameter for the duration of the ice cover was set to 2 months, between early January and early March. During this time, gas exchange was set to zero.

Although $v_{g,600}$ can be fairly well estimated from wind speed, it may be interesting to treat it as a free parameter and look for the optimum value to fit the observations. An independent estimate of the gas exchange velocity could be important for the assessment of fluxes of gases such as O_2 or CO_2 into and from the lake. Thus, the standard scenario model was run with $v_{g,600}$ as a free parameter in addition to the $K(z)$ -profile and the He flux. The optimum was achieved at $v_{g,600} = (0.32 \pm 0.06) \text{ m day}^{-1}$. The reduction of $v_{g,600}$ from the mean value of 0.55 m day^{-1} is compensated mainly by a decreased He flux (2.05 instead of $2.28 \times 10^{-8} \text{ cm}^3 \text{ STP m}^{-2} \text{ s}^{-1}$). The fit is very slightly improved by these changes (χ^2 is reduced from 406 to 399). As before with the parameters for seasonal mixing, the optimization of the gas exchange parameter indicates that a somewhat weaker turnover of gases in the mixolimnion than assumed in the standard scenario would yield slightly better fits to the data. However, the improvements are very small.

4.7. Flux of mantle He

He originates from natural sources (dissolution of atmospheric air, production of radiogenic He from U and Th decay in the crust, flux of He from the mantle). Therefore it can be assumed that the He input is constant over time and that the He profile is at steady state. The steady state assumption is further justified by many observations. For instance, temperature and He concentration in the monimolimnion did not change measurably between 1994 and 1996. Even the oldest temperature data from the monimolimnion (Olivier, 1952; Pelletier, 1968) agree with our CTD data within the limits of their accuracy. Michard et al. (1994) and Viollier et al. (1995, 1997) used the steady state assumption to calculate element fluxes in the monimolimnion, and justified it by the agreement of their results for several geochemical parameters with previous data.

Hence, in contrast to the transient tracers tritium and CFCs, for which a non-stationary model of the complete evolution since 1940 is necessary, for He it would be sufficient to find the steady state solution of the model. In practice, He was also modeled as a time-dependent variable, using the measured concentrations from 1994 as initial conditions for 1940 to assure rapid convergence to the steady state. As for the transient tracers, it was assumed that the He concentration of all inflows to the mixolimnion (Q_p , Q_r , and Q_{45}) is in equilibrium with the atmosphere, which was calculated according to Weiss (1971). This assumption may be questionable for Q_{45} , because groundwaters usually have an excess of atmospheric as well as terrigenous He components (Aeschbach-Hertig et al., 1999b; Kipfer et al., 2002). However, since neither the He nor the Ne profiles provide clear indications for the presence of such excess components, it is reasonable to assume that they are unimportant for the He balance in view of the large excesses of mantle He in deeper layers of the lake.

The observation of a large excess of mantle He in the monimolimnion of Lac Pavin implies the presence of a strong He source from under ground. There are two principal possibilities how this He can be transported into the lake. If there is a spring in the monimolimnion, it may act as the single point source of He because of a high He concentration in the spring water. Thus, the concentration of He in the deep spring ($C_{\text{He},85}$) must be a free parameter in such scenarios. In scenarios with no spring in the monimolimnion, the input of He is assumed to be unrelated to sublacustrine springs and uniformly distributed over the entire sediment area, thus entering both the mixo- and the monimolimnion. The He flux per unit sediment area (F_{He}) is introduced as a free parameter in these models.

Both types of He input are certainly simplified pictures of the geological reality, since Lac Pavin is situated in a complex environment of volcanic deposits (e.g., Camus et al., 1993). However, for the 1-D model used here, only the vertical distribution of the He input and not its precise location is relevant. The question of the distribution and origin of He and CO_2 flux in Lac Pavin was addressed in more detail in Aeschbach-Hertig et al. (1999a).

The flux of He could not be quantified very precisely in the framework of the simple box model used by Aeschbach-Hertig et al. (1999a). Thus, the respective conclusions of that study may be refined with the more detailed model used here. The determination of

the He flux from the model is based on the assumption that the He concentrations in the monimolimnion are at steady state. If this assumption holds, the He input flux must be balanced by vertical transport across the chemocline. Thus, the calculated He flux into the monimolimnion depends strongly on the vertical diffusivity in the chemocline.

As discussed above, all scenarios without a significant deep spring yield very well constrained results for K_{chemo} , and hence also for the He flux F_{He} . The large He gradient in the chemocline is the most distinct feature of all measured profiles, and therefore provides the most restrictive constraints for the related parameters. All scenarios yield values around $2.2 \times 10^{-8} \text{ cm}^3 \text{ STP m}^{-2} \text{ s}^{-1}$ ($1.0 \times 10^{-12} \text{ mol m}^{-2} \text{ s}^{-1}$) for F_{He} (Table 5). This result is in exact agreement with the estimate obtained from the box model of Aeschbach-Hertig et al. (1999a), but its uncertainty is reduced from $\pm 30\%$ to about $\pm 10\%$. The ^4He (or total He) fluxes can be converted to ^3He fluxes using the constant isotope ratio of the inflowing He component (9.09×10^{-6}) to yield a ^3He flux of $2.0 \times 10^{-13} \text{ cm}^3 \text{ STP m}^{-2} \text{ s}^{-1}$. Finally, following the reasoning of Aeschbach-Hertig et al. (1999a) that at least 78% of the CO_2 in the monimolimnion are of magmatic origin, and that the C^3He ratio of the magmatic source is 13×10^9 , we can calculate a magmatic CO_2 flux of $1.2 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$. However, the uncertainty of this flux estimate is not much reduced from the original $\pm 40\%$, because the CO_2 concentrations were measured only with a precision of $\pm 20\%$ and because the splitting of the CO_2 in a magmatic and biogenic component adds additional uncertainty.

The inferred flux of magmatic CO_2 is equivalent to a yearly CO_2 release of 72 tons from Lac Pavin, 70 times less than at Laacher See (Aeschbach-Hertig et al., 1996b), and several orders of magnitude less than the amount of CO_2 that was instantaneously released during the catastrophe at Lake Nyos in 1986 (Kling et al., 1987). As long as the monimolimnion of Lac Pavin remains at steady state with respect to the input of magmatic CO_2 , no further accumulation of CO_2 occurs and hence no danger of catastrophic degassing exists.

4.8. CFC degradation rates

Both the literature on CFC degradation and the vanishing concentrations in the monimolimnion strongly suggest that CFCs are consumed in the anoxic deep water of Lac Pavin. Oster et al. (1996) determined

CFC degradation rates in several natural anoxic environments, including groundwaters and the bottom layer of a small pond. They found a large range of absolute values of the zero-order degradation rate, but a constant ratio between the rates of CFC-11 and CFC-12 degradation, the former always being 10 times higher than the latter. Typical degradation rates in groundwater were $1 \text{ pmol l}^{-1} \text{ year}^{-1}$ for CFC-11 and $0.1 \text{ pmol l}^{-1} \text{ year}^{-1}$ for CFC-12. In the pond, the rates were more than two orders of magnitude larger. Shapiro et al. (1997) modeled CFC-degradation in a Norwegian fjord as a first-order process, and obtained degradation rates of $6\text{--}9 \text{ year}^{-1}$ for CFC-11, and less than 0.03 year^{-1} for CFC-12. Bullister & Lee (1995) found CFC-11 degradation rates of 0.26 to 0.48 year^{-1} in the Black Sea and 0.9 year^{-1} in a Canadian fjord. In view of the large range of literature values, it seems that CFC degradation rates should be treated as free parameters in the model of Lac Pavin.

However, first tests with the model showed that even the low rates observed by Oster et al. (1996) in groundwaters were sufficient to keep the modeled concentrations in the monimolimnion below the detection limit. Since degradation takes place only in the anoxic layers of the monimolimnion and the chemocline, and the water exchange across the chemocline is limited, a further increase of the degradation rates has very little effect on the modeled CFC profiles. Therefore, the degradation rates were usually kept fixed at the above mentioned 'groundwater' values. Model runs to optimize the degradation rates were made only after the other model parameters, particularly the diffusion in the chemocline, had been determined.

If in the standard model only the zero-order CFC-degradation rates were treated as fit parameters, with the $K(z)$ profile fixed at the values given in Table 5, the following results were obtained: $(0.7 \pm 0.1) \text{ pmol kg}^{-1} \text{ year}^{-1}$ for CFC-11 and $(0.07 \pm 0.04) \text{ pmol kg}^{-1} \text{ year}^{-1}$ for CFC-12. These values are in good agreement with the results obtained by Oster et al. (1996), in particular in view of the 10:1 ratio between the degradation rates of the two species. The magnitude of the rates is in the range observed for groundwaters. Alternatively, CFC degradation was also modeled with a first order degradation rate. The resulting rates were $(0.6 \pm 0.1) \text{ year}^{-1}$ for CFC-11 and $(0.11 \pm 0.04) \text{ year}^{-1}$ for CFC-12. The result for CFC-11 is in good agreement with the rates reported by Bullister & Lee (1995).

In contrast to the studies of Bullister & Lee (1995) and Shapiro et al. (1997) it seems that the CFC-12 data

from Lac Pavin are not compatible with zero CFC-12 degradation. The standard scenario without CFC-12 degradation predicts clearly measurable concentrations (about 0.3 pmol kg^{-1}) in the monimolimnion. Yet, our constraints on the water balance and mixing of Lac Pavin may not be sufficient to unequivocally prove the presence of anaerobic CFC-12 degradation. Alternative hypotheses helping to explain the absence of CFC-12 in the monimolimnion may be the existence of a small input of CFC-free water, non-stationary mixing conditions (i.e., decreasing deep water renewal during the last decades, when CFC input increased), or removal of CFCs by scavenging.

5. Conclusions

The application of a broad set of tools of modern physical limnology, including high resolution CTD profiles, transient and geochemical tracers (tritium, CFCs, He), and numerical modeling, allowed us to clarify the physical structure and dynamics of Lac Pavin. A 3-D survey of CTD data indicates the existence of a sublacustrine spring at about 45 m depth, i.e., above rather than below the chemocline. Furthermore, the CTD data provide the basis for a stability analysis of the water column, which shows that the chemocline is strongly stabilized by the increase of dissolved solids, indicating that vertical turbulent mixing is likely very low in that layer. Quantification of the vertical turbulent diffusivity becomes possible in the framework of a 1-D vertical lake model, which simulates the evolution of transient tracer distributions over the past 50 years.

The approach of determining physical parameters by inverse modeling is complicated by ambiguities about the surface water input of the lake, and in particular the depth and size of sublacustrine springs. Moreover, it was not possible to unequivocally reconstruct the local tritium input function and the tritium concentrations of the sublacustrine springs. Therefore, the water input to the mixolimnion – both at the surface and from the sublacustrine spring indicated by the CTD data – cannot be precisely determined. Our best estimates are 18 l s^{-1} for the water input by direct rain, and 20 l s^{-1} for surface water runoff, but the latter number has a large uncertainty. The spring at about 45 m depth discharges on the order of 10 l s^{-1} of cold, fresh water. We assume that the water of this spring contains more or less modern concentrations of tritium, and deduce that the tritium concentrations

in the surface water input are reduced to one half of the tritium concentrations measured in precipitation at Thonon-les-Bains. However, it cannot be excluded that the spring water is free of transient tracers and the tritium concentrations in the surface water input are less reduced relative to the Thonon record.

In general, physical processes that influence the concentrations in the deep water are more strongly constrained by the observed data from two different years but only one season than processes in the mixolimnion. The model is not very sensitive to parameters such as the duration of seasonal mixing or the gas exchange velocity. However, the data provide strong indications that complete seasonal mixing does not penetrate the entire mixolimnion, but only the uppermost 30 m. Vertical turbulent diffusivity in the thermocline and hypolimnion are in the expected range between 10^{-6} and $10^{-5} \text{ m}^2 \text{ s}^{-1}$.

The distinct gradients of all observed concentrations, and particularly of He, in the chemocline prove most useful to constrain the free parameters in the deep water. Most importantly, the constraints imposed by the observed tritium and He profiles allow us to exclude the previous hypothesis of a significant spring in the monimolimnion. Moreover, the vertical turbulent diffusivity in the chemocline can be precisely determined. The turbulent diffusive transport across the chemocline is strongly suppressed, with a mean value of the diffusivity between 60 and 70 m depth of $5 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$. This very low value is almost a factor of three below the molecular diffusivity of heat, thus implying that heat transport through the chemocline is dominated by molecular mechanisms. This surprising finding provides an explanation for the elevated temperature in the monimolimnion without the need of a special heat source, such as a thermal spring. A normal geothermal heat flow of $30\text{--}40 \text{ mW m}^{-2}$ is entirely sufficient to produce the observed temperature anomaly.

With respect to dissolved species, the low turbulent diffusivity in the chemocline leads to residence times of nearly 100 years in the stagnant monimolimnion. Given this long residence time, the elevated concentrations of He, CO_2 , and many other dissolved constituents can be explained by moderate fluxes, which can be estimated with a precision of about 10%. The results for He and CO_2 are $1.0 \times 10^{-12} \text{ mol m}^{-2} \text{ s}^{-1}$ and $1.2 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1}$, respectively. The inferred yearly release of 72 tons of CO_2 from Lac Pavin is small compared to other volcanic lakes. Another consequence of the long residence time in the monim-

olimnion is that relatively low CFC degradation rates of $0.7 \text{ pmol kg}^{-1} \text{ year}^{-1}$ for CFC-11 and $0.07 \text{ pmol kg}^{-1} \text{ year}^{-1}$ for CFC-12 are sufficient to remove any CFCs that are transported into the monimolimnion by diffusion.

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References

- Aeschbach-Hertig, W., 1994. Helium und Tritium als Tracer für physikalische Prozesse in Seen. Diss. ETH Nr. 10714, ETH Zürich, 272 pp.
- Aeschbach-Hertig, W., R. Kipfer, M. Hofer, D. M. Imboden & H. Baur, 1996a. Density-driven exchange between the basins of Lake Lucerne (Switzerland) traced with the ^3H - ^3He method. *Limnol. Oceanogr.* 41: 707–721.
- Aeschbach-Hertig, W., M. Hofer, R. Kipfer, D. Imboden & R. Wieler, 1999a. Accumulation of mantle gases in a permanently stratified volcanic Lake (Lac Pavin, France). *Geochim. Cosmochim. Acta* 63: 3357–3372.
- Aeschbach-Hertig, W., R. Kipfer, M. Hofer, D. M. Imboden, R. Wieler & P. Signer, 1996b. Quantification of gas fluxes from the subcontinental mantle: The example of Laacher See, a maar lake in Germany. *Geochim. Cosmochim. Acta* 60: 31–41.
- Aeschbach-Hertig, W., F. Peeters, U. Beyerle & R. Kipfer, 1999b. Interpretation of dissolved atmospheric noble gases in natural waters. *Water Resour. Res.* 35: 2779–2792.
- Alvinerie, J., B. Dégot, P. Lévêque & M. Vigneaux, 1966. Activité en tritium et caractéristiques chimiques des eaux du lac Pavin. *C. r. Acad. Sci. Paris* 262 D: 846–849.
- Beyerle, U., R. Kipfer, D. M. Imboden, H. Baur & T. Graf, 2000. A mass spectrometric system for the analysis of noble gases from water samples. *Envir. Sci. Technol.* 34: 2042–2050.
- Bullister, J. L. & B.-S. Lee, 1995. Chlorofluorocarbon-11 removal in anoxic marine waters. *Geophys. Res. Lett.* 22: 1893–1896.
- Busenberg, E., E. P. Weeks, L. N. Plummer & R. C. Bartholomay, 1993. Age dating ground water by use of chlorofluorocarbons (CCl_3F and CCl_2F_2), and distribution of chlorofluorocarbons in the unsaturated zone, Snake River plain aquifer, Idaho National Engineering Laboratory, Idaho. USGS Water Resources Investigations Report Nr. 93–4054, United States Geological Survey.
- Camus, G., G. Michard, P. Olive, P. Boivin, P. Desgranges, D. Jézéquel, M. Meybeck, J.-C. Peyrus, J.-M. Vinson, E. Viollier & J. Kornprobst, 1993. Risques d'éruption gazeuse carbonique en Auvergne. *Bull. Soc. géol. France* 164: 767–781.
- Chen, C. T. & F. J. Millero, 1986. Precise thermodynamic properties for natural waters covering only the limnological range. *Limnol. Oceanogr.* 31: 657–662.
- Clark, J. F. & G. B. Hudson, 2001. Quantifying the flux of hydrothermal fluids into Mono Lake by use of helium isotopes. *Limnol. Oceanogr.* 46: 189–196.
- Clark, J. F., P. Schlosser, R. Wanninkhof, H. J. Simpson, W. S. F. Schuster & D. T. Ho, 1995. Gas transfer velocities for SF_6 and ^3He in a small pond at low wind speeds. *Geophys. Res. Lett.* 22: 93–96.
- Clarke, W. B., W. J. Jenkins & Z. Top, 1976. Determination of tritium by mass spectrometric measurement of ^3He . *Int. J. appl. Radiat. Isotopes* 27: 515–522.
- Delebecque, A., 1898. Les lacs français. Chamerot & Renouard, Paris, 436 pp.
- Dunai, T. J. & H. Baur, 1995. Helium, neon, and argon systematics of the European subcontinental mantle: Implications for its geochemical evolution. *Geochim. Cosmochim. Acta* 59: 2767–2783.
- Elkins, J. W., T. M. Thompson, T. H. Swanson, J. H. Butler, B. D. Hall, S. O. Cummings, D. A. Fisher & A. G. Raffo, 1993. Decrease in the growth rates of atmospheric chlorofluorocarbons 11 and 12. *Nature* 364: 780–783.
- Glaudeaud, P., 1916. Le cratère-lac du Pavin et le volcan de Montchalm. *C. r. Acad. Sci. Paris* 162: 428–430.
- Hofer, M. & D. M. Imboden, 1998. Simultaneous determination of CFC-11, CFC-12, N_2 and Ar in water. *Anal. Chem.* 70: 724–729.
- Hohmann, R., R. Kipfer, F. Peeters, G. Piepke, D. M. Imboden & M. N. Shimaraev, 1997. Processes of deep water renewal in Lake Baikal. *Limnol. Oceanogr.* 42: 841–855.
- IAEA, 1992. Statistical treatment of data on environmental isotopes in precipitation. Technical Reports Series Nr. 331, IAEA, Vienna, 781 pp.
- IAEA/WMO, 2001. Global network of isotopes in precipitation. The GNIP database. <http://isohis.iaea.org>.
- Imboden, D. M. & A. Wüest, 1995. Mixing mechanisms in lakes. In Lerman, A., D. M. Imboden & J. R. Gat (eds), *Physics and Chemistry of Lakes*. Springer, Berlin: 83–138.
- Imboden, D. M., R. F. Weiss, H. Craig, R. L. Michel & C. R. Goldman, 1977. Lake Tahoe geochemical study. 1. Lake chemistry and tritium mixing study. *Limnol. Oceanogr.* 22: 1039–1051.
- Imboden, D. M., U. Lemmin, T. Joller, K. H. Fischer & W. Weiss, 1981. Lake mixing and trophic state. *Verh. int. Verein. Limnol.* 21: 115–119.
- Imboden, D. M., U. Lemmin, T. Joller & M. Schurter, 1983. Mixing processes in lakes: Mechanisms and ecological relevance. *Schweiz. Z. Hydrol.* 45: 11–44.
- Khalil, M. A. K. & R. A. Rasmussen, 1989. The potential of soils as a sink of chlorofluorocarbons and other man-made chlorocarbons. *Geophys. Res. Lett.* 16: 679–682.
- Kipfer, R., W. Aeschbach-Hertig, H. Baur, M. Hofer, D. M. Imboden & P. Signer, 1994. Injection of mantle type helium into Lake Van (Turkey): The clue for quantifying deep water renewal. *Earth planet. Sci. Lett.* 125: 357–370.
- Kipfer, R., W. Aeschbach-Hertig, F. Peeters & M. Stute, 2002. Noble gases in lakes and ground waters. In Porcelli, D., C. Ballentine & R. Wieler (eds), *Noble Gases in Geochemistry and Cosmochemistry*. *Rev. Miner. Geochem.* 47: 615–700.
- Kling, G. W., M. A. Clark, H. R. Compton, J. D. Devine, W. C. Evans, A. M. Humphrey, E. J. Koenigsberg, J. P. Lockwood, M. L. Tuttle & G. N. Wagner, 1987. The 1986 Lake Nyos gas disaster in Cameroon, West Africa. *Science* 236: 169–175.
- Krause, W. J., 1980. Tritium-Bilanzierung kleiner Einzugsgebiete in der Eifel, Teil I – Wasserbilanz. *Dtsche Gewässerkundl. Mitt.* 24: 2–14.
- Kuhn, W., 1977. Berechnung der Temperatur und Verdunstung alpiner Seen auf klimatologisch-thermodynamischer Grundlage.

- Arbeitsberichte der Schweizerischen Meteorologischen Zentralanstalt Nr. 70, Schweizerische Meteorologische Zentralanstalt, Zürich, 33 pp.
- Li, Y.-H., 1973. Vertical eddy diffusion coefficient in Lake Zürich. Schweiz. Z. Hydrol. 35: 1–7.
- Lovley, D. R. & J. C. Woodward, 1992. Consumption of freons CFC-11 and CFC-12 by anaerobic sediments and soils. *Envir. Sci. Technol.* 26: 925–929.
- Maloszewski, P. & A. Zuber, 1982. Determining the turnover time of groundwater systems with the aid of environmental tracers. I. Models and their applicability. *J. Hydrol.* 57: 207–231.
- Martin, J.-M., 1985. The Pavin Crater Lake. In Stumm, W. (ed.), *Chemical Processes in Lakes*. John Wiley & Sons, New York: 169–188.
- Meybeck, M., J. M. Martin & P. Olive, 1975. Géochimie des eaux et des sédiments de quelques lacs volcaniques du Massif Central français. *Verh. int. Ver. Limnol.* 19: 1150–1164.
- Michard, G., E. Viollier, D. Jézéquel & G. Sarazin, 1994. Geochemical study of a crater lake: Pavin Lake, France – Identification, location and quantification of the chemical reactions in the lake. *Chem. Geol.* 115: 103–115.
- Montzka, S. A., J. H. Butler, R. C. Myers, T. M. Thompson, T. H. Swanson, A. D. Clarke, L. T. Lock & J. W. Elkins, 1996. Decline in the tropospheric abundance of halogen from halo-carbons: Implications for stratospheric ozone depletion. *Science* 272: 1318–1322.
- Oliver, B. M., H. Farrar IV & M. M. Bretscher, 1987. Tritium half-life measured by helium-3 growth. *Appl. Radiat. Isot.* 38: 959–965.
- Olivier, L., 1952. Sur la présence en été, dans le lac Pavin, d'une couche dépourvue d'oxygène, vers 70 m de profondeur. *C. r. Acad. Sci. Paris* 234: 743–745.
- Oster, H., C. Sonntag & K. O. Münnich, 1996. Groundwater age dating with chlorofluorocarbons. *Water Resour. Res.* 32: 2989–3001.
- Peeters, F., G. Piepke, R. Kipfer, R. Hohmann & D. M. Imboden, 1996. Description of stability and neutrally buoyant transport in freshwater lakes. *Limnol. Oceanogr.* 41: 1711–1724.
- Peeters, F., R. Kipfer, R. Hohmann, M. Hofer, D. M. Imboden, G. G. Kodenev & T. Khozder, 1997a. Modelling transport rates in Lake Baikal: gas exchange and deep water renewal. *Envir. Sci. Technol.* 31: 2973–2982.
- Peeters, F., G. Piepke & M. Gloor, 1997b. A diffusion model for the development of a boundary layer in lakes. *Aquat. Sci.* 59: 95–114.
- Peeters, F., R. Kipfer, D. Achermann, M. Hofer, W. Aeschbach-Hertig, U. Beyerle, D. M. Imboden, K. Rozanski & K. Fröhlich, 2000. Analysis of deep-water exchange in the Caspian Sea based on environmental tracers. *Deep-Sea Res.* 47: 621–654.
- Pelletier, J.-P., 1968. Un lac meromictique, le Pavin (Auvergne). *Annales de la Station Biol. Besse-en-Chandesse* 3: 147–170.
- Reichert, P., 1994. AQUASIM – a tool for simulation and data analysis of aquatic systems. *Wat. Sci. Tech.* 30: 21–30.
- Restituito, F., 1987. Consequences of redox conditions on the distribution of cations in a meromictic oligotrophic lake. *Hydrobiologia* 144: 63–75.
- Rozanski, K., R. Gonfiantini & L. Araguas-Araguas, 1991. Tritium in the global atmosphere: Distribution patterns and recent trends. *J. Phys. G: Nucl. Part. Phys.* 17: S523–S536.
- Schmid, M., 1997. Physikalische und chemische Prozesse im Lac Pavin: Ursachen und Folgen der stabilen Schichtung eines vulkanischen Kratersees. Diploma thesis, ETH Zürich, 93 pp.
- Shapiro, S. D., P. Schlosser, W. M. Smethie & M. Stute, 1997. The use of ^3H and tritogenic ^3He to determine CFC degradation and vertical mixing rates in Framvaren Fjord, Norway. *Mar. Chem.* 59: 141–157.
- Torgersen, T., Z. Top, W. B. Clarke, W. J. Jenkins & W. S. Broecker, 1977. A new method for physical limnology – tritium-helium-3 ages – results for Lakes Erie, Huron and Ontario. *Limnol. Oceanogr.* 22: 181–193.
- Upstill-Goddard, R. C., A. J. Watson, P. S. Liss & M. I. Liddicoat, 1990. Gas transfer velocities in lakes measured with SF_6 . *Tellus* 42B: 364–377.
- Van Senden, D. C., R. Portielje, A. Borer, H. Ambühl & D. M. Imboden, 1990. Vertical exchange due to horizontal density gradients in lakes; the case of Lake Lucerne. *Aquat. Sci.* 52: 381–398.
- Viollier, E., D. Jézéquel, G. Michard, M. Pèpe, G. Sarazin & P. Albéric, 1995. Geochemical study of a crater lake (Pavin Lake, France): Trace-element behaviour in the monimolimnion. *Chem. Geol.* 125: 61–72.
- Viollier, E., G. Michard, D. Jézéquel, M. Pèpe & G. Sarazin, 1997. Geochemical study of a crater lake: Lake Pavin, Puy de Dôme, France. Constraints afforded by the particulate matter distribution in the element cycling within the lake. *Chem. Geol.* 142: 225–241.
- Wanninkhof, R., 1992. Relationship between wind speed and gas exchange over the ocean. *J. Geophys. Res.* 97: 7373–7382.
- Wanninkhof, R., J. Ledwell & J. Crusius, 1990. Gas transfer velocities on lakes measured with sulfur hexafluoride. In Wilhelms, S.C. & J. S. Gulliver (eds), *Air–Water Mass Transfer*. Amer. Soc. Civil Eng., New York: 441–458.
- Warner, M. J. & R. F. Weiss, 1985. Solubilities of chlorofluorocarbons 11 and 12 in water and seawater. *Deep-Sea Res.* 32: 1485–1497.
- Weiss, R. F., 1971. Solubility of helium and neon in water and seawater. *J. Chem. Eng. Data* 16: 235–241.
- Weiss, R. F., E. C. Carmack & V. M. Koropalov, 1991. Deep-water renewal and biological production in Lake Baikal. *Nature* 349: 665–669.
- Weiss, W., J. Bullacher & W. Roether, 1979. Evidence of pulsed discharges of tritium from nuclear energy installations in Central European precipitation. In *Behaviour of tritium in the environment* (San Francisco, 16–20 October, 1978), IAEA, Vienna: 17–30.
- Welander, P., 1968. Theoretical forms for the vertical exchange coefficients in a stratified fluid with application to lakes and seas. *Geophys. Gothoburg.* 1: 1–27.
- Wüest, A., W. Aeschbach-Hertig, H. Baur, M. Hofer, R. Kipfer & M. Schurter, 1992. Density structure and tritium-helium age of deep hypolimnetic water in the northern basin of Lake Lugano. *Aquat. Sci.* 54: 205–218.
- Wüest, A., G. Piepke & J. D. Halfman, 1996. Combined effects of dissolved solids and temperature on the density stratification of Lake Malawi. In Johnson, T. C. & E. O. Odada (eds), *The Limnology, Climatology and Paleoclimatology of the East African Lakes*, Gordon & Breach, Toronto: 183–202.