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Impact of lake level change on deep-water renewal and oxic conditions in deep saline Lake Van, Turkey

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[1] Changes in the hydrological regime of the saline closed basin Lake Van, a large, deep lake in eastern Turkey, resulted in a lake level increase by about 2 m between 1988 and 1995, followed by a 1.5 m decrease until 2003 and a relatively constant lake level thereafter. Based on measurements of transient tracers (sulfur hexafluoride, CFC-12, ^{3}H, ^{3}He, ^{4}He, Ne), dissolved oxygen, light transmission, conductivity-temperature-depth profiles, and thermistor data, we investigate the implications associated with lake level fluctuations for deep-water renewal and oxygenation. Our data suggest that deep-water renewal was significantly reduced in Lake Van between 1990 and 2005. This change in mixing conditions resulted in the formation of a more than 100 m thick anoxic deep-water body below 325 m depth. Apparently, the freshwater inflows responsible for the lake level rise between 1988 and 1995 decreased the salinity of the surface water sufficiently that the generation of density plumes during winter cooling was substantially reduced compared to that in the years before the lake level rise. Significant renewal and oxygenation of the deep water did not occur until at least 2005, although by 2003 the lake level was back to almost the same level as in 1988. This study suggests that short-term changes in the hydrological regime, resulting in lake level changes of a couple of meters, can lead to significant and long-lasting changes in deep-water renewal and oxic conditions in deep saline lakes.

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1. Introduction

[2] Mixing processes in saline closed basin lakes, mostly located in arid or semiarid climates, are very susceptible to changes in climatic conditions [*Hammer*, 1986; *Lemcke and Sturm*, 1997]. Especially changes in the hydrological regime in catchments and associated changes in freshwater inflow affect the density stratification in saline lakes and, thus, influence the conditions required for the generation of density plumes and convective deep-water renewal [*Peeters and Kipfer*, 2009]. In the case of the Caspian Sea the lake level rise between the late 1970s and the mid 1990s, resulting from enhanced freshwater inflow from the Volga River, was associated with low deep-water oxygen levels. Hydrographic data and measurements of transient tracers suggested that the low oxygen concentrations were the result of a significant reduction in the deep-water exchange during the time of the lake level rise [*Peeters et al.*, 2000a]. At Mono Lake increased runoff between 1982 and 1984, in 1986, and between 1995 and 1999 resulted in two periods of large lake level rise and caused stable density stratification due to increased salinity gradients. As a consequence, vertical mixing and nutrient transport were considerably reduced, and Mono Lake became meromictic between 1983 and 1988 and, again, from 1995 until at least 2001, respectively [*Jellison and Melack*, 1993, 2001; *Melack and Jellison*, 1998]. After the onset of lake level decline in 1986, it was another 2.5 years until deep-water exchange started again [*Jellison and Melack*, 1993].

[3] Here we investigate how mixing conditions and oxic state in deep (450 m) closed basin Lake Van (Turkey) were affected during a recent period (1989–2008) of lake level change. Lake Van is of particular interest for studying changes in deep-water conditions associated with lake level variations for the following reasons.

[4] a. The high salinity of Lake Van water (21 g kg^{-1}) makes mixing conditions in Lake Van very sensitive to lake level fluctuations. Especially in highly saline lakes, freshwater inflows connected to lake level rise can cause a significant increase in density stratification and, as a consequence, affect the key mechanisms causing deep-water

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renewal: turbulent mixing and the generation of density plumes.

[5] b. Detailed data on hydrography and on transient tracers are available from a study that focused specifically on deep-water mixing in Lake Van [*Kipfer et al.*, 1994]. The fieldwork for this older study was conducted in 1989 and 1990, at the onset of the recent lake level rise, and therefore provides excellent background information for the interpretation of our data collected after the lake level rise.

[6] c. Lake Van has been selected as an International Continental Scientific Drilling Program drilling site, and at the end of 2010 sediment records will be available that cover about 500,000 years [*Litt et al.*, 2007] of sediment history. Within the last 20,000 years the lake level in Lake Van was more than 70 m higher [*Landmann et al.*, 1996] and up to 260 m lower [*Landmann et al.*, 1996; *Lemcke*, 1996; *Wick et al.*, 2003] than today. According to *Landmann et al.* [1996], several periods of fast lake level rise occurred, during which the lake level increased by about 200 m within about 1000 years. On the basis of the Ca/Mg ratio in sediments, *Wick et al.* [2003] concluded that after the last major drop in lake level, by more than 250 m, the salinity returned to its original value within less than 50 years, suggesting a lake level rise of more than 200 m within 50 years. Thus, an understanding of the consequences of lake level change for mixing conditions and oxic state in Lake Van may be important for the interpretation of sedimentation and proxies stored in the sediments [see, e.g., *Verschuren*, 1999] and will be particularly relevant in investigations focusing on remains of lakeborne organisms, for example, studies on resting eggs of cladocerans, which we found to be preserved for at least 1000 years in Lake Van sediments.

[7] Deep-water exchange in deep lakes usually results from vertical turbulent diffusion and from density plumes, which often propagate downward at lake boundaries [*Peeters and Kipfer*, 2009]. Several processes generating density plumes have been identified to have caused significant mixing in deep lakes: river inflows in Lake Baikal and Lake Geneva [*Hohmann et al.*, 1997; *Lambert and Giovanoli*, 1988], interbasin exchange in Lake Baikal, the Caspian Sea, and Lake Lucerne [*Hohmann et al.*, 1997; *Peeters et al.*, 2000a; *Aeschbach-Hertig et al.*, 1996], differential cooling in Lake Geneva and Lake Issyk-Kul [*Fer et al.*, 2001; *Peeters et al.*, 2003], thermal bar mixing in Lake Ontario, Lake Baikal, and Lake Ladoga [*Rogers*, 1966; *Shimaraev et al.*, 1993; *Malm and Mironov*, 1994; *Hohmann et al.*, 1997], transport due to thermobaric instabilities in Lake Baikal [*Weiss et al.*, 1991; *Wüest et al.*, 2005], and wind-driven downwelling in combination with the thermobaric effect in Crater Lake, Oregon, and Lake Baikal [*Crawford and Collier*, 2007; *Schmid et al.*, 2008].

[8] At Lake Van freshwater inflows from rivers are not able to generate density plumes that can penetrate to the deep water because of the high salinity of Lake Van water. Its high salinity is also responsible for the very low temperature at maximum density, $T_{\mathrm{md}} = -1.3°\mathrm{C}$, and surface pressure [*Kempe*, 1977]. Because surface and deep-water temperatures are above the T_{md} all year round, except perhaps in very shallow near-shore areas, thermal-bar mixing and thermobaric instabilities do not play a significant role in deep-water renewal. Hence, the main processes that could be responsible for deep-water renewal in saline Lake Van are restricted to turbulent mixing and density plumes associated with differential cooling, interbasin exchange, and convection due to surface cooling and evaporation.

[9] Transport processes resulting from density plumes are usually localized and often occur only sporadically, making in situ observation and, especially, quantification of exchange rates rather difficult. Whereas CTD (conductivity, temperature, depth) profiles and data on dissolved oxygen and light transmission can support the identification of the relevant transport processes causing deep-water mixing [e.g., *Hohmann et al.*, 1997, 1998; *Peeters et al.*, 2003; *Peeters and Kipfer*, 2009], transient tracers such as ^{3}He, ^{3}H, chlorofluorocarbons (CFCs), and sulfur hexafluoride (SF_6) have been used in several studies to quantify deep-water exchange in large lakes, for example, ^{3}H-^{3}He, and CFCs in Lake Baikal [*Weiss et al.*, 1991; *Hohmann et al.*, 1998; *Peeters et al.*, 2000b] and in the Caspian Sea [*Peeters et al.*, 2000a], ^{3}H-^{3}He, SF_6, and CFCs in Lake Issyk-Kul [e.g., *Hofer et al.*, 2002], and ^{3}H-^{3}He and SF_6 in Lake Lugano [*Aeschbach-Hertig et al.*, 2007].

[10] However, only *Peeters et al.* [2000a] have employed transient tracer and CTD data to discuss the consequences of lake level rise on deep-water renewal. To our knowledge, this study on Lake Van is the first in which transient tracer and CTD data are available from the time before and after a lake level rise. In 1989 and 1990 mixing processes in Lake Van were investigated, based on CTD measurements and vertical profiles of ^{3}H and dissolved noble gases Ne, ^{3}He, and ^{4}He [*Kipfer et al.*, 1994]. According to *Kipfer et al.* [1994], deep-water renewal in 1989 and 1990 was rapid, and complete exchange of deep water for surface water occurred within 1–2 years. This deep-water exchange was suggested by ^{3}H-^{3}He water ages and by an inverse simulation of the vertical distribution of ^{3}He, ^{4}He, and ^{3}H using a one-dimensional vertical transport model [*Kipfer et al.*, 1994]. However, both techniques required an assumption about the terrigenic ^{3}He/^{4}He ratio.

[11] After the study by *Kipfer et al.* [1994], the level of Lake Van has increased by 1.5 m over 6 years and then decreased again to a slightly lower level than in 1989–1990. To investigate whether this variation in lake level had an effect on mixing rates and on the ecological state of Lake Van, we collected new data from Lake Van between 2004 and 2008. This data set not only provides new measurements of the tracers already investigated by *Kipfer et al.* [1994], but also includes profiles of the transient tracers CFC-12 and SF_6. Interpretation of the new data set in light of the data from 1989–1990 is the central focus of the research presented here.

[12] In the following we first provide more detailed information on the study site and on what is known about lake level changes in Lake Van. Then we describe fieldwork and methods employed to analyze water samples and CTD profiles. Results from the new field campaigns are presented and compared to the data of *Kipfer et al.* [1994] from 1990. In section 5 these results are interpreted with respect to deep-water renewal, suggesting that during the recent increase in lake level by only 1.5 m, deep-water renewal was significantly reduced, resulting in a more than 100 m deep, anoxic deep-water body in Lake Van.

2. Study Site, Lake Van

[13] Lake Van (Figure 1) is a saline closed basin lake (pH ~9.7; salinity, ~21 g kg^{-1}), located in eastern Anatolia,

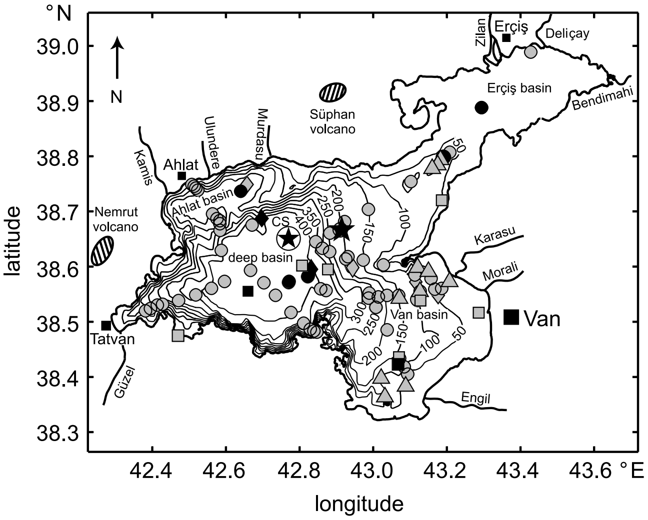

Figure 1. Bathymetric map of Lake Van with sampling stations from August 2004 (diamond), May and September 2005 (circles), February and March 2006 (triangles), July 2006 (squares), and September 2008 (CS): conductivity-temperature-depth (CTD) station (gray symbols), water sampling and CTD station (black symbols), mooring positions (black star), and central station (CS; circle with black star). Water samples in May and September 2005 and CTD profiles in May and September 2005, July 2006, and July 2008 were taken at the CS, and the mooring 2006/2007 and 2007/2008 was installed. Isobaths were calculated by two-dimensional linear interpolation of 900 depth measurements which we digitized from the map of Lake Van of 1983 (*Türkiye Doku Anadolu Van Gölü*, 1985, Department of Hydrology and Oceanography, Istanbul, chart no. 9008). The isobaths and the shore line correspond to a lake surface level of 1646 m above sea level.

Turkey, at an altitude of 1649 m above sea level (43°E, 38.5°N). It is the largest lake in Turkey (surface area, ~3522 km^2; volume, ~576 km^3 [*Landmann et al.*, 1996]) and also the world's largest soda lake, with a maximum depth of about 450 m. In Lake Van four basins are usually distinguished: the shallow Erçis basin in the northeast, the Van basin in the southeast, the Ahlat basin in the northwest, and the deep basin (>400 m) in the center of the lake. However, the basins are horizontally connected and not separated by sills, except for the Ahlat basin, which is separated by a sill reaching depths of up to ~110 m. Between 1968 and 1970 the level of Lake Van (Figure 2) rose by about 1 m, and between December 1988 and June 1995 it increased by an additional 2 m. From 1995 to 2003 the level decreased by about 1.5 m, to the level of 1989, and remained at that level until 2006. Seasonally, the water level fluctuates by up to 0.9 m (time period of observation: 1944–2006), typically reaching an annual maximum in late spring-early summer (main period of rain and snowmelt) and an annual minimum in autumn-winter due to high evaporation and low input by rivers and precipitation during summer. According to *Kadıoğlu et al.* [1997] and *Kılınçaslan* [2000], the recent changes in the annual lake level are linked to climatic change.

[14] Sediment cores and lake terraces indicate that during the Last Glacial Maximum (~19,000 years B.P.) the lake level was more than 70 m higher [*Landmann et al.*, 1996] and that during the Younger Dryas (~10,500 years B.P) the lake level was about 260 m lower [*Landmann et al.*, 1996; *Lemcke*, 1996; *Wick et al.*, 2003] than today. The 260 m lake level decrease occurred within 1500 years [*Wick et al.*, 2003] and was followed by a dramatic increase, of about 200 m, in less than 1200 years [*Landmann et al.*, 1996]. Based on the Mg/Ca ratio in sediments, *Wick et al.* [2003] concluded that the lake level increase was significantly faster than suggested by *Landmann et al.* [1996] because salinity levels had returned to values before the lake level drop within a time period of only 50 years. These substantial lake level fluctuations were caused by hydrometeorological changes [e.g., *Kempe*, 1977; *Degens and Kurtmann*, 1978; *Landmann et al.*, 1996].

3. Field Campaigns and Methods

3.1. Field Campaigns and Sampling

[15] The data presented here were collected during seven field campaigns to Lake Van between 2004 and 2008 (August 2004, May and September 2005, February, March, and July 2006, and September 2008). During all field campaigns CTD profiles were taken (Figure 1). In 2004 and 2006 a water sample profile was collected for tracer analysis (^{3}H, ^{3}He, ^{4}He, and Ne) in the deep basin of Lake Van. During the two field campaigns in 2005, water for analysis of the transient tracers (SF$_6$, ^{3}H, ^{3}He, ^{4}He, CFC-12, and noble gases), major ions, and nutrients was sampled at various depths and at different positions in Lake Van. In 2005 in the deep basin a water sample profile was collected for determination of the dissolved oxygen concentration. Water samples were taken using Niskin bottles. On board the water for SF$_6$ and CFC-12 analysis was transferred into 500 ml stainless steel cylinders and closed off [*Hofer et al.*, 2002]. Water samples for ^{3}H and noble gas analysis were collected in copper tubes according to the technique described by *Beyerle et al.* [2000].

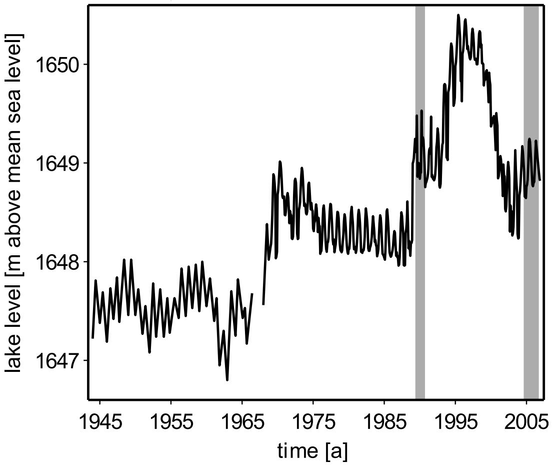

Figure 2. Lake level data between 1944 and 2006 measured at staff gauge of the Tatvan discharge measurement station by the Elektrik İşleri Etüt İdaresi. From 1944 to 1968 maximum and minimum lake levels are available for each year except 1967 [*Kempe*, 1977]. Monthly data are available for all years from 1969 to 2006. Gray bars indicate times of different field campaigns.

Table 1. Empirical Coefficients for Calculation of the Practical Salinity from Temperature (°C), Conductivity (mS cm^{-1}), and Pressure (dbar) for Lake Van Water Using the *UNESCO* Equations for Calculation of Salinity from the Conductivity Ratio [*UNESCO, SCOR, IAPSO*, 1981][a]

$a_0 = 1.3462 \times 10^{-2}$	$b_0 = 5.1365 \times 10^{-4}$	$c_0 = 5.9452 \times 10^{-1}$
$a_1 = -1.9957 \times 10^{-1}$	$b_1 = -7.5714 \times 10^{-3}$	$c_1 = 1.7393 \times 10^{-2}$
$a_2 = 20.653$	$b_2 = -4.1192 \times 10^{-3}$	$c_2 = 1.2858 \times 10^{-4}$
$a_3 = 21.179$	$b_3 = -5.1267 \times 10^{-2}$	$c_3 = -1.1638 \times 10^{-6}$
$a_4 = -6.3472$	$b_4 = 5.0995 \times 10^{-2}$	$c_4 = 8.3937 \times 10^{-10}$
$a_5 = 1.2805$	$b_5 = -2.7942 \times 10^{-3}$	

[a] The absolute salinity of Lake Van water was assumed to be 21 g kg^{-1}.

3.2. Conductivity-Temperature-Depth (CTD) Measurements

[16] Vertical profiles of temperature (T), electrical conductivity (C), pressure (p), dissolved oxygen saturation (O_2), pH, light transmission, and chlorophyll *a* concentration were recorded in situ with an Ocean Seven 320 CTD multiparameter probe (IDRONAUT S.r.l), additionally equipped with a 25 cm pathlength C Star Transmissiometer (WET Labs) and a Seapoint chlorophyll *a* fluorometer (resolution: pressure, 0.01 dbar; temperature, 0.0001°C; conductivity, 0.1 μS cm^{-1}; dissolved oxygen, 0.01 mg L^{-1}; pH 0.001; light transmission, 0.1%; and chlorophyll *a* fluorescence, 0.01 μg L^{-1}). Additional profiles of CTD were measured using a CTD plus 500 probe (SiS Sensoren Instrumente Systeme GmbH; temperature, 0.001°C; pressure, 0.01 dbar; conductivity, 1 μS cm^{-1}). More than 90 high-resolution CTD profiles were taken at different stations during the field campaigns on Lake Van.

[17] Absolute salinity (S) was calculated from CTD data using a modification of the United Nations Educational, Scientific and Cultural Organization [*UNESCO, SCOR, IAPSO*, 1981] formula for practical salinity in sea water, taking into account the ionic composition of Lake Van. Following the procedure described by *Peeters et al.* [2003] the temperature dependence of conductivity in Lake Van waters was determined in the laboratory by measuring C, T, and p at a known S using the Ocean Seven 320 CTD multiparameter probe (IDRONAUT S.r.l) with a short-circuited pumping system and a cooling and heating system to vary the water temperature. The dependence of conductivity on total ion concentration was considered by conducting similar measurements using Lake Van water diluted with deionized water to 100%, 97.5%, 95%, 92.5%, 90%, 87.5%, and 85% Lake Van water. The salinity of undiluted Lake Van water was determined from major ion analysis to be $S = 21$ g kg^{-1} ± 10%. To account for the physicochemical properties of Lake Van water, the empirical coefficients a_i, b_i, c_i, and k of UNESCO equations, describing the dependence of conductivity on temperature and ion concentration, were modified by least-squares minimization between the salinity obtained using the UNESCO algorithm and the absolute salinity from the water chemistry [*Peeters et al.*, 2003] (Table 1). The pressure dependence of conductivity was assumed to be the same as in oceanic waters (i.e., the respective coefficients [*UNESCO, SCOR, IAPSO*, 1981] were not modified).

[18] The density for Lake Van water (ρ_{Van}) was calculated by using the equation of state for seawater [*UNESCO, SCOR, IAPSO*, 1981] with a modification to account for the ionic composition of Lake Van water, as described by *Peeters et al.* [2000a]:

$$\rho_{\mathrm{Van}}(T,S,p) = \rho_{\mathrm{sea}}(T,S=0,p) + f[\rho_{\mathrm{sea}}(T,S,p) - \rho_{\mathrm{sea}}(T,S=0,p)], \tag{1}$$

where ρ_{sea} is the density function of seawater and $f = 1.0465$ is the correction factor estimated for the ion composition of Lake Van water. Potential density is defined with the lake surface as the reference depth, $\rho_{\mathrm{pot}} = \rho_{\mathrm{Van}}(\theta, S, p = 0)$, and θ is the potential temperature.

[19] The influence of temperature and salinity on the stability of the water column was calculated from temperature and salinity profiles [*Gill*, 1982]:

$$N^2 = N_T^2 + N_S^2, \quad \text{with} \quad N_T^2 = g\alpha\left(\frac{dT}{dz} + \Gamma\right), \quad N_S^2 = -g\beta_S\frac{dS}{dz}, \tag{2}$$

where N^2 is the square of the stability frequency (s^{-2}), and N_T^2 and N_S^2 are the contributions to N^2 from temperature and salinity gradients, respectively. T is the in situ water temperature (°C), g is the gravitational acceleration (m s^{-2}), α is the thermal expansion coefficient (°C^{-1}), β_S is the haline contraction coefficient (kg g^{-1}), Γ is the adiabatic lapse rate (°C m^{-1}), S is the salinity (g kg^{-1}), and z is the water depth (m; positive upward). Following the procedure described by *Peeters et al.* [2000a] we obtained an average haline contraction coefficient of $\beta_S = 0.775 \times 10^{-3}$ kg g^{-1}.

[20] The oxygen sensor measures oxygen as percentage saturation and was calibrated to 100% saturation in air prior to the measurements. Oxygen concentrations were calculated from the measured oxygen saturation using the solubility of oxygen [*Weiss*, 1970] at in situ temperature and salinity and at air pressure. In September 2005 the oxygen sensor was not adequately calibrated and therefore the calculated oxygen concentrations were corrected by scaling the O_2 concentrations of the upper 15 m such that they agreed with the O_2 equilibrium concentration at this depth. The correction factor was 0.8. In addition to the sensor measurements, dissolved oxygen was measured by Winkler titration in selected water samples.

3.3. Data From Moorings

[21] From September 2005 to July 2006 a mooring was installed at position 38°39.968′N and 42°54.857′E, where the water depth is about 200 m (Figure 1). The mooring was equipped with 17 thermistors (8 RBR TR-1050, 9 Vemco Minilog) and two current meters (Aanderaa RCM 7). The temperature sensors were installed at between 1 and 150 m depth, with a typical spacing of 1–5 m in the upper 30 m and a spacing of 10–25 m below 30 m depth. The Aanderaa current meters were located at depths of 10 and 100 m. The instruments collected data at time intervals of 15 s (RBR thermistors), 25 to 75 min (Vemco thermistors), and 60 min (Aandera current meters).

[22] Additionally, a mooring was installed from July 2006 to July 2007 (19 thermistors: 2 RBR TR-1050, 17 Vemco Minilog; position, 38°38.058′N, 42°46.124′E; maximum water depth, 445 m) and from September 2007 to September 2008 (23 thermistors; 4 RBR TR-1050, 19 Vemco Minilog; position, 38°38.037′N, 42°46.345′E; maximum water depth, 442 m). In the upper 150 m the spacing of the temperature

Table 2. Major Ion Composition of Lake Van Water in the Deep Basin for July 1974, June 1990, and May and September 2005[a]

Date	Na^+ (mg L^{-1})	K^+ (mg L^{-1})	Ca^{2+} (mg L^{-1})	Mg^{2+} (mg L^{-1})	Cl^- (mg L^{-1})	SO_4^{2-} (mg L^{-1})	HCO_3^- (mg L^{-1})	CO_3^{2-} (mg L^{-1})	Salinity (g kg^{-1})
July 1974									
Mean water column	7747	508	5–10	94.8	5450	2344	2191	3331	21.3
June 1990 (stations 27–28/90)[b]									
Mean water column	7912	430	3.8	110	5812	2408	3149	1717	21.2
Mean hypolimnion	7972	433	3.6	110	5871	2435	3306	1773	21.5
May 2005									
Mean water column	8177	425	<10	112	6104	2526	2310	1439	20.7
Mean hypolimnion	8209	428	<10	112	6144	2537	2314	1442	20.8
September 2005									
Mean water column	7452	485	<10	119	6322	2763	2691	1680	21.2
Mean hypolimnion	7511	488	<10	120	6191	2778	2696	1683	21.1

[a] Data for July 1974 were taken from *Kempe* [1977] and data for June 1990 were from *Reimer et al.* [1992]. Mean values for the hypolimnion were calculated for the depth interval between 100 m and lake bottom on the basis of chemical data of one water profile for each date.

[b] From *Reimer et al.* [1992].

sensors was similar to that in the previously installed mooring. Additional sensors were mounted at depths of 200, 400, and 440 m in 2006–2007 and depths of 190, 405, and 430 m in 2007–2008. The instruments collected data at time intervals of 15 s (RBR thermistors) or of 30 or 60 min (Vemco thermistors).

3.4. Transient Tracer

[23] SF_6 and CFC-12 concentrations were analyzed in the same water sample using gas chromatography and an electron capture detector following *Hofer et al.* [2002]. The overall error of the method is 5% [*Hofer et al.*, 2002]. The detection limit of this method is 0.01 pg kg^{-1} for SF_6 and 0.24 pg kg^{-1} for CFC-12.

[24] SF_6 and CFC-12 water ages were calculated by comparing the concentration of the respective tracer in the water sample with its historic atmospheric equilibrium concentration [*IAEA*, 2006; *Kipfer et al.*, 2002]. These age calculations assume that the transient gases were in equilibrium with the gas concentrations in the atmosphere at in situ water temperature, water salinity, and the atmospheric pressure at the lake surface (0.82 atm). A source of error in these age calculations could be that atmospheric gases can be introduced into the water, not only by equilibration, but also by air injection via gas bubbles, for example, due to wave breaking. This so-called "excess air" can be estimated from the concentration of excess Ne, the difference between the measured Ne concentration and the Ne concentration in atmospheric equilibrium at in situ temperature, salinity, and atmospheric pressure at the lake surface [see, e.g., *Kipfer et al.*, 2002].

[25] ^3H, ^3He, ^4He, and Ne were determined by mass spectrometric method as described by *Beyerle et al.* [2000]. ^3H was measured by the ^3He ingrowth method [*Clarke et al.*, 1976]. The measuring precision is 5.2% for ^3H concentration, 1.0% for ^3He concentration, and 1.6% for Ne concentration. ^3H-^3He water ages (τ) are calculated using the following equation [*Torgersen et al.*, 1977]:

$$\tau = \frac{1}{\lambda} \ln\left(1 + \frac{^3He_{tri}}{^3H}\right), \qquad (3)$$

where $\lambda = 0.05576$ [*Taylor and Roether*, 1982] is the decay constant of trititum and $^3He_{tri}$ is the concentration of tritiogenic ^3He. $^3He_{tri}$ is determined from the data on ^3He, ^4He, and $^3He/^4He$ using the technique described by *Kipfer et al.* [2002]: $^3He_{tri} = {}^4He_m(R_m - R_{ter})^{-4}He_{eq}(R_{eq} - R_{ter})$, where ^4He_m is the measured ^4He concentration, R_m is the measured $^3He/^4He$ ratio, R_{ter} is the terrigenic $^3He/^4He$ ratio, $^4He_{eq}$ is the equilibrium concentration of ^4He, and R_{eq} is the equilibrium $^3He/^4He$ ratio. On the basis of the neon data, the occurrence of significant amounts of excess air can be excluded. The atmospheric equilibrium concentration of ^3He ($^3He_{eq}$) and ^4He was calculated using the helium solubility given by *Weiss* [1971] and the fractionation factor between ^3He and ^4He given by *Benson and Krause* [1980]. In the calculations that follow we compare the consequences of assuming two different ratios of terrigenic helium: $(^3He/^4He)_{ter} = 1 \times 10^{-5}$ and $(^3He/^4He)_{ter} = 5 \times 10^{-6}$, respectively.

[26] The uncertainty of τ was estimated using error propagation calculation including the measuring errors of ^3H, ^3He, ^4He, and the $^3He/^4He$ ratio and assuming an error of 0.5% for $^3He_{eq}$ and $^4He_{eq}$ [*Weiss*, 1971] and of 0.4% for λ [*Aeschbach-Hertig*, 1994]. The uncertainty in $(^3He/^4He)_{ter}$ was not included in the error calculation, since we wanted to investigate the effect of the two different values of $(^3He/^4He)_{ter}$ mentioned on the ^3H-^3He water ages obtained. The mean averages and the standard deviation of τ for different depth regions were estimated.

4. Results

4.1. Water Chemistry

[27] The ionic composition measured in water samples from May and September 2005 is shown in Table 2. Within our overall experimental error of 10% for individual measurements, the ionic compositions as well as the absolute concentrations were the same as measured in 1974 [*Kempe*, 1977] and in 1990 [*Reimer et al.*, 1992, 2009]. From the chemical data the absolute salinity of Lake Van waters was determined to be 21.0 g kg^{-1}, with a standard deviation of 0.3 g kg^{-1}, in the deep water, below 100 m depth.

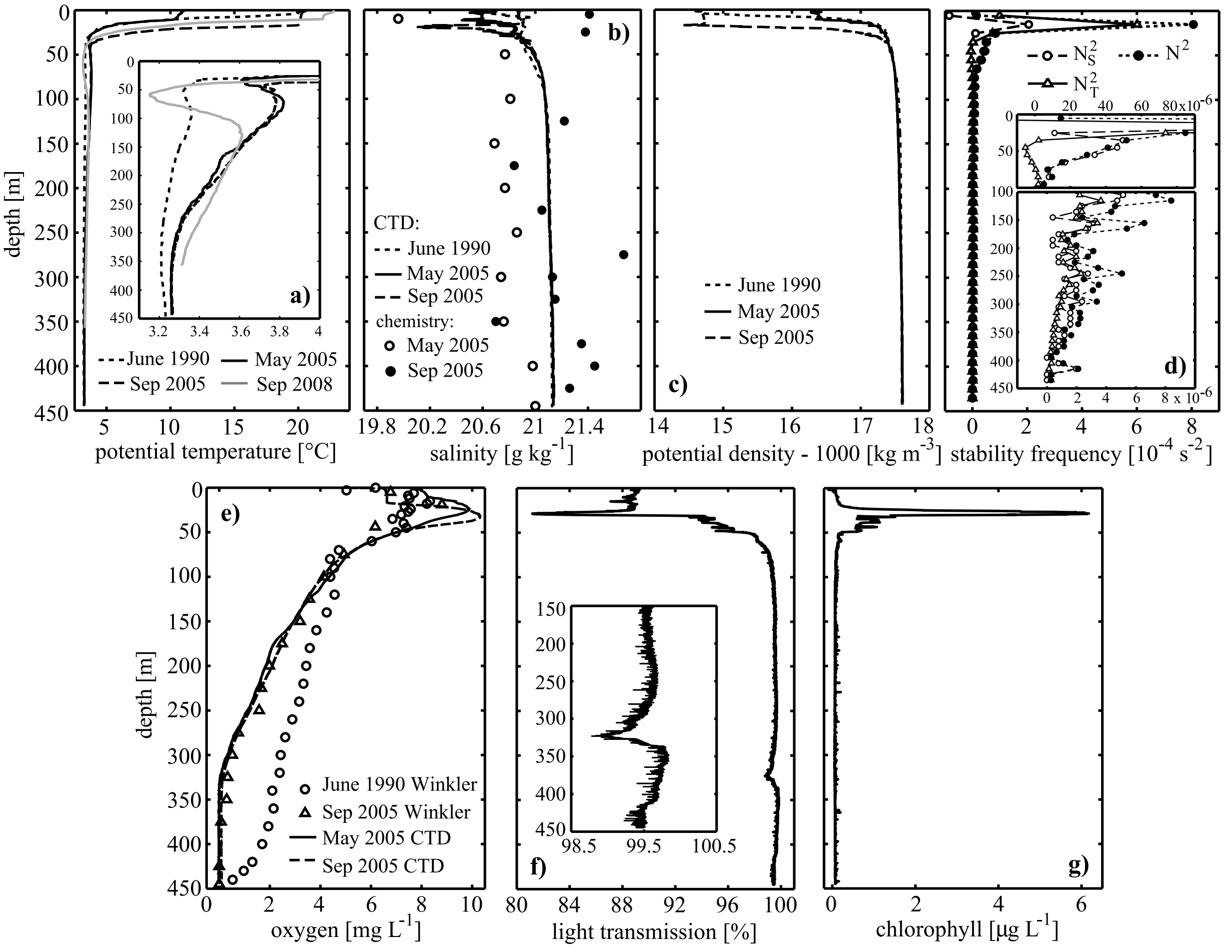

Figure 3. (a) Potential temperature (CTD: June 1990, May and September 2005, September 2008), (b) salinity (CTD: 1990; CTD + chemical analysis: May and September 2005), (c) potential density (CTD: June 1990, May and September 2005), (d) Brunt Väisälä frequency (CTD: May 2005), (e) dissolved oxygen concentration (CTD: May and September 2005; Winkler titration: June 1990 and September 2005), (f) light transmission (CTD: May 2005), and (g) chlorophyll a (CTD: May 2005) as a function of depth.

4.2. CTD Measurements and Thermistor Data

[28] Figure 3 presents vertical profiles of potential temperature θ, salinity S, potential density ρ_{pot}, stability frequency N^2, dissolved oxygen concentration, light transmission, and chlorophyll *a* concentration from the central station of the deep basin of Lake Van. Data shown were collected in May and September 2005 and also include temperature and dissolved oxygen concentrations measured in 1990 [*Kipfer et al.*, 1994] and a temperature profile from September 2008 (only 0–350 m depth).

4.2.1. Potential Temperature

[29] In May and September 2005 the potential temperature decreased from the surface down to about 30 and 40 m depth, respectively, then it increased again until a depth of about 70 m, resulting in a characteristic temperature minimum between about 30–45 and 40–45 m depth, respectively (Figure 3a). The vertical position of this minimum is deeper at locations with a lesser water depth than at deep stations. Below 70 m depth, the temperature decreased with increasing depth down to 380 m, reaching a minimum value of 3.28°C (Figure 3a). In the deepest water layer, below 380 m depth, the temperature increased slightly toward the lake bottom. Horizontal differences in the deep-water temperatures were small, for example, less than 0.03°C at 300 m depth.

[30] All temperature profiles measured in summer and fall between 2004 and 2008 showed a strong temperature decrease at between 10 and 40 m, suggesting a similar location of the main thermocline during the stratified season. All CTD profiles from 2005 and 2006 as well as the temperature data from the mooring installed in 2005–2006 indicate that, between May 2005 and July 2006, temperature changes larger than 0.2°C, caused by seasonal or diurnal variations in water temperature, occurred only above 70 m depth. Data from the moored thermistors (Figure 4) indicate that the lowest temperatures in the upper 60 m occurred in the second half of February and in March 2006 but were always above 3.5°C. Temperatures at 70 m depth were always higher than this value. Below 70 m depth the observed small temperature fluctuations are periodic in nature, suggesting internal wave activity.

[31] In 2005 and 2006, water temperatures at all depths below the thermocline were higher than in 1990 (Figure 3a). In 2008 temperatures below 100 m were also higher than in 1990. The characteristic temperature minimum, however,

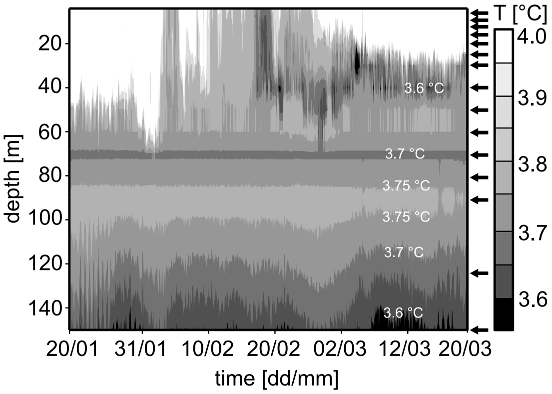

Figure 4. Temperature measured by the moored thermistors located at 38°39.968′N and 42°54.857′E. The period from 20 January 2006 to 20 March 2006 is shown. dd/mm, day/month. Arrows mark the depths where the thermistors were installed.

was significantly colder in 2008 than in 2005 and 1990 (0.5° and 0.2°C colder, respectively) and was also located at a greater depth, ~60 m (Figure 3a), than in the earlier years. Note that the cold water at the characteristic minimum is associated with sufficiently low salinity that the profile is stably stratified and no convection can occur locally. Unfortunately, the CTD profile in 2008 did not extend down to the lake bottom, and thus, it is impossible to draw conclusions from this profile about deep-water intrusions. The moored thermistors indicated cold-water intrusions between 70 and 90 m depth with a minimum temperature of 2.8°C in February and April 2008. A thermistor located at about 400 m depth near the lake bottom did not show clear signs of cold water intrusions but indicated a general linear warming trend in the deep water from 2006 to January 2008. However, after January 2008 the temperature increase in the deep water during winter-spring was higher than before.

4.2.2. Salinity

[32] Below the thermocline, salinity calculated from the CTD measurements increased with increasing depth (Figure 3b). In May 2005 at deep open-water stations, the salinity in the upper 20 m was at least 0.5 g kg^{-1} lower than in the deep water. In September 2005 the salinity in the upper 16 m was higher than in May 2005, because in the summer months water input by rivers and precipitation is lower and evaporation is higher than in the winter and spring months. Below 30 m, salinity in September was the same as in May 2005 (Figure 3b). Salinity estimated from the chemical composition measured in water samples had an overall experimental error of ±2 g kg^{-1}, and thus, it is not suitable to investigate vertical salinity gradients in Lake Van, but it supported the absolute value of salinity used in the calibration of salinity from conductivity.

[33] The salinity in the upper 10 m is strongly influenced by the vicinity of rivers and gradually increases with increasing distance from the river mouths toward the deep basin. Therefore marked horizontal salinity gradients were observed in the surface water of Lake Van. In May 2005, salinity in the surface water was 2.5 g kg^{-1} lower in the shallow Erçis basin of Lake Van than in the open water (CTD and chemistry data). The Ercis basin receives freshwater input from the large rivers Bendimahi and Zilan, which enter the lake in the northeast and have the highest discharge during April to June, due to snowmelt and precipitation in the catchments. Not only in Ercis basin but also at other river mouths, salinity was significantly lower than in the open water of Lake Van. The large salinity fluctuations in the strong thermocline at between 16 and 21 m depth may indicate intrusions of Ercis basin or river water. However, the salinity fluctuations could also be an artifact arising from the conversion of in situ conductivity to salinity at a very slight shift between temperature and conductivity measurements.

4.2.3. Potential Density and Stability

[34] In 1990 and in May and September 2005 the potential density increased monotonically below the thermocline (Figure 3c). In 2005, at most depths the vertical gradients in temperature and salinity both stabilized the water column (Figure 3d). In the thermocline the contribution to stability by the vertical temperature gradient was much larger than the contribution by the salinity gradient. However, in the depth range between the local temperature minimum and the local temperature maximum, the contribution of the vertical temperature gradient to stability was negative. Nevertheless, the water column was still stably stratified, because the vertical gradient in salinity was sufficient to compensate for the destabilizing effect of the inverse temperature gradients (Figures 3b and 3d). In September 2008 the water column below the surface mixed layer was also stably stratified, and the potential density increased monotonically with increasing depth.

[35] Note that the salinity gradients contributed significantly to the difference in potential density between surface water and deep water. Even in summer, when temperatures reached 20°C in surface waters and deep-water temperatures remained at about 3°C, the salinity difference of 0.5 g kg^{-1} between surface and deep water accounts for 15% of the difference in potential density. At surface temperatures below 8°C a salinity difference of 0.5 g kg^{-1} becomes the dominant factor for density stratification.

4.2.4. Dissolved Oxygen

[36] In May 2005 oxygen in the surface water was close to atmospheric equilibrium. The oxygen concentration increased with increasing depth down to about 30 m (Figure 3e), where a local O$_2$ maximum (~106% saturation) was observed, probably in response to primary production. Below the O$_2$ maximum the oxygen concentration continuously decreased with increasing depth. No oxygen was detectable at below 325 m depth, with a range of ±10 m in depth, depending on the position in the lake. All oxygen profiles from May and September 2005 showed anoxic conditions at below 325 m water depth. Oxygen measurements based on Winkler titration agreed very well with the data from the CTD probe and confirmed anoxia in the entire deep-water body, below 325 m, in 2005. Fifteen years earlier, in June 1990, the deep water was not anoxic but dissolved O$_2$ concentrations were 2.4 mg L^{-1} at 320 m and 0.6 mg L^{-1} at 440 m [*Reimer et al.*, 1992] (Figure 3e).

4.2.5. Light Transmission and Chlorophyll *a* Fluorescence

[37] The profile of light transmission (Figure 3f) has a distinct minimum at about 325 m depth. In all CTD profiles from deep stations a minimum was observed at a similar depth that always coincided with the transition from oxic to anoxic conditions. This turbid layer may be caused by precipitation of iron and manganese minerals in the oxic/

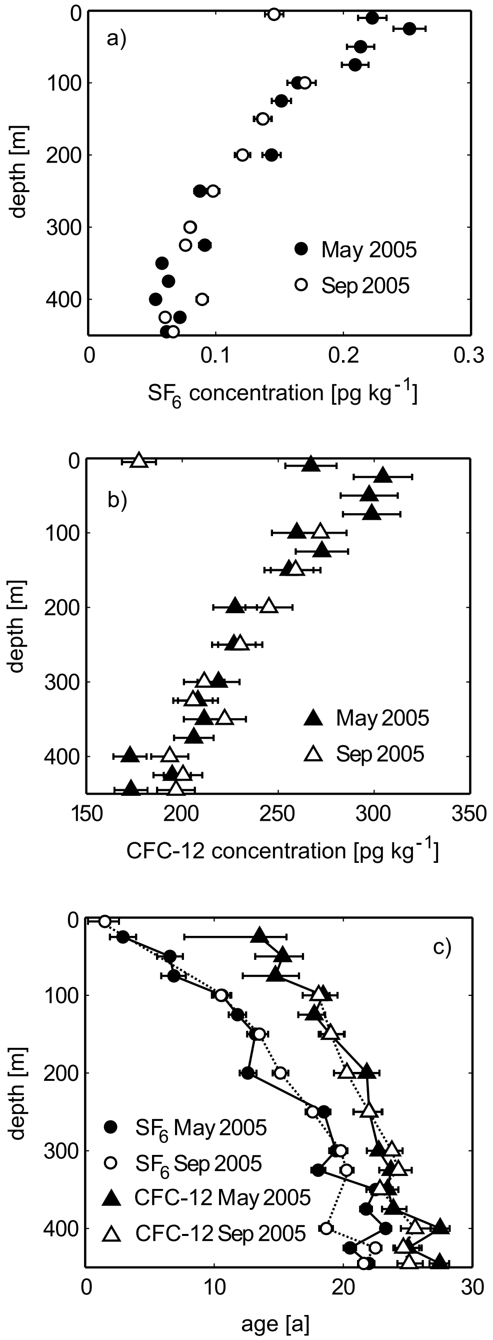

Figure 5. Profiles of sulfur hexafluoride (SF_6) and chlorofluorocarbon (CFC-12) concentrations and resulting apparent water ages for May and September 2005. (a, b) Error bars indicate 5% errors of concentration measurements. (c) Error bars depict the range between the minimum and the maximum SF_6 age and CFC-12 age, respectively, assuming a ±5% error in the tracer concentration. Error bars include neither the uncertainty of the atmospheric concentrations nor the consequences of mixing within the water column.

anoxic transition zone, as observed, for example, in the Black Sea [*Sorokin*, 2002]. The profile of light transmission has a second minimum at a depth of about 30 m, which coincides with a maximum in chlorophyll *a* fluorescence and a broad peak in dissolved oxygen (Figures 3e–3g), suggesting that the minimum in the light transmission profile at 30 m depth is due to algae.

4.3. Transient Tracers

[38] Below the thermocline the concentrations of the tracers SF_6 and CFC-12 decreased with increasing depth (Figure 5). Because the water temperature was almost constant in the deeper water, below 100 m, the tracer concentrations in the deep water reflect the change in atmospheric concentration at the time of the last gas/water partitioning. At the same depth below the thermocline, tracer concentrations from May and September 2005 were very similar. In the upper 30 m the tracer concentrations decreased toward the lake surface, because the water temperatures increased toward the lake surface, and the solubility of SF_6 and CFC-12 decreased strongly with increasing temperature, resulting in degassing of SF_6 and CFC-12 to the atmosphere during the summer months.

[39] All measured neon concentrations were close to or slightly lower than the atmospheric equilibrium concentration at in situ temperature and atmospheric pressure (undersaturated by up to 5%), suggesting that direct air injection is small in Lake Van. Hence, in the calculation of apparent water age from tracer concentrations, we assumed that the influence of excess air is negligible.

[40] SF_6 and CFC-12 apparent water age increased with increasing depth (Figure 5c). In the anoxic water layer (below 325 m), the apparent water age was nearly constant, with an average value of 22 ± 1 years for SF_6 and 25 ± 2 years for CFC-12 in 2005. The systematic differences between the SF_6 and the CFC-12 apparent water ages can be explained by the different shapes of the atmospheric input curves for these tracers. In the case of CFC-12 the atmospheric concentration increased nearly linearly between 1970 and 1990 and nonlinearly thereafter, reaching a maximum in 2001. Therefore, mixing of water with different CFC-12 concentrations results in CFC-12 water ages that are larger than the isolation age, that is, the CFC-12 water age overestimates the time elapsed since the water was last in contact with the atmosphere [*Hofer et al.*, 2002]. In the case of SF_6 the atmospheric concentrations increased nearly linearly. Therefore, the SF_6 water age is a more reliable measure of the isolation age than the CFC-12 water age and will be used henceforth to estimate exchange rates and residence times in Lake Van. The difference in tracer water age between the surface and the deep water can be used as an estimate of the deep-water residence time [*Peeters et al.*, 2000a]. Because the average SF_6 water age was about 5 ± 3 years in the upper 100 m and about 22 ± 1 years in the anoxic deep-water layer, the SF_6 data from 2005 suggest that the average residence time of the anoxic deep water is about 17 ± 3 years (Table 4).

[41] ^{3}He concentrations below 150 m were significantly higher in 2004 to 2006 than in 1990 (Figure 6a). The volume-weighted mean ^{3}He concentration below 200 m was 0.99 × 10^{-13} cm^3 STP (standard temperature and pressure: T_0 = 273.15 K = 0°C, p_0 = 1 atm) g^{-1} in 1990 and 1.17 × 10^{-13} cm^3 STP g^{-1} in 2005 (Table 3). In the upper 200 m the ^{3}He concentration was about the same in 1990 and 2005 (7.1 × 10^{-14} cm^3 STP g^{-1}; Table 3). In contrast to the increase in ^{3}He concentrations in deep waters and to the unchanged values in the upper 200 m, all ^{3}H concentrations measured in water samples collected in 2004 to 2006 were significantly

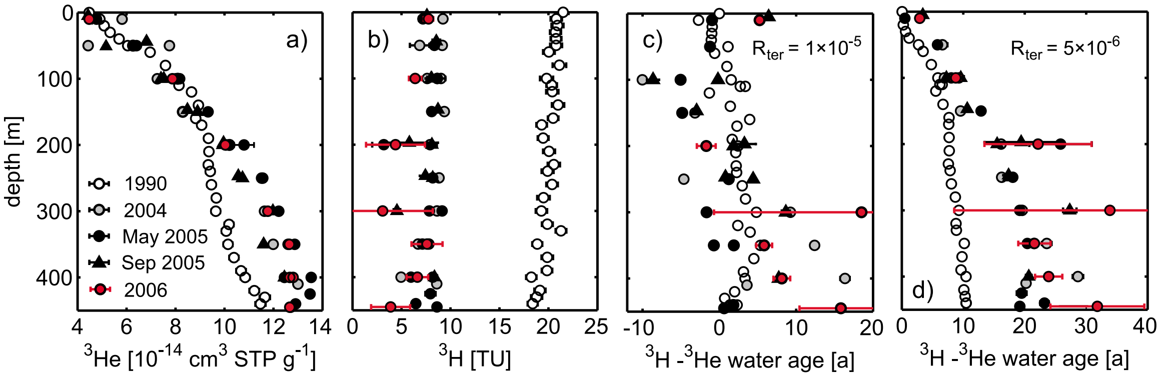

Figure 6. Comparison of vertical profiles of (a) ^{3}He and (b) ^{3}H concentrations and ^{3}H-^{3}He water ages for water samples collected in (c, d) 1990 and 2004–2006. ^{3}H-^{3}He water ages τ were calculated assuming (c) $(^3He/^4He)_{ter} = 1 \times 10^{-5}$ and (d) $(^3He/^4He)_{ter} = 5 \times 10^{-6}$, respectively. Error bars were calculated considering the uncertainties in measured tracer concentrations, atmospheric equilibrium concentrations of ^{3}He and ^{4}He, and the decay constant λ. (c, d) Sensitivity of τ to the assumption on $(^3He/^4He)_{ter}$.

lower than the ^{3}H values reported for 1990 (Figure 6b). The volume-weighted mean concentration of ^{3}H below 200 m in Lake Van was 19.8 TU (tritium units) in 1990 and 7.6 TU in 2005 (Table 3). In the water layer above 200 m the corresponding values were 20.5 TU and 8.5 TU, respectively.

[42] Water ages calculated from ^{3}H and ^{3}He are highly uncertain because of the large terrigenic helium component. *Kipfer et al.* [1994] assumed terrigenic helium to have $(^3He/^4He)_{ter} = 1 \times 10^{-5}$, a ratio that was observed in the nearby crater lake Nemrut and that is characteristic for mantle-type helium [*Lupton*, 1983]. They arrived at their value of $(^3He/^4He)_{ter}$ by extrapolation of a mixing line in a $^3He/^4He$–$^{20}Ne/^4He$ diagram. However, recent measurements in Lake Van sediments suggest that their value of $(^3He/^4He)_{ter}$ was too high. Using the value $(^3He/^4He)_{ter} = 1 \times 10^{-5}$ of *Kipfer et al.* [1994], the calculation of ^{3}H-^{3}He water ages from the data obtained for water samples from 2005 provides very low ^{3}H-^{3}He water ages, many of them even negative (Figure 6c). Hence, these ^{3}H-^{3}He water ages do not seem very plausible and are significantly smaller than the SF$_6$ water ages for the same water samples, although one would expect rather good agreement between the water ages derived from ^{3}H-^{3}He and SF$_6$ [see *Hofer et al.*, 2002]. The unexpectedly low or even negative ^{3}H-^{3}He water ages (Figure 6c) suggest that the tritiogenic ^{3}He component is underestimated and hence the $(^3He/^4He)_{ter}$ is most likely too high. ^{3}H-^{3}He water ages can be made to agree with SF$_6$ water ages if the terrigenic helium component is assumed to have a ratio of $(^3He/^4He)_{ter} = 5 \times 10^{-6}$ between mantle- and crustal-type helium. Using $(^3He/^4He)_{ter} = 5 \times 10^{-6}$ the ^{3}H-^{3}He water age below 325 m was 10 ± 0.5 years in 1990 and increased to 22 ± 3 years in 2005 (Figure 6d and Table 4), suggesting reduced deep-water exchange during that time period. The corresponding estimates of deep-water residence times are 8 ± 2 years in 1990 and 17 ± 5 years in 2005 (Table 4).

Table 3. Volume-Weighted Mean Concentrations of ^{3}H, ^{3}He, and O$_2$ and Volume-Weighted Mean Temperature (*T*) in the Deep-Water Body, Below 200 m, 1990 and May 2005

Year	^{3}H (TU)	^{3}He (10^{-14} cm^3 STP g^{-1})[a]	O$_2$(10^{11} g)	*T*(°C)
1990	19.8	9.9	4.4	3.24
2005	7.6	11.7	1.1	3.34

[a] STP, standard temperature and pressure.

5. Discussion

[43] Vertical profiles of potential temperature, dissolved oxygen, ^{3}He, and water ages suggest that deep-water renewal was significantly reduced between 1990 and 2005. The following discussion provides arguments supporting the hypothesis that between 1990 and 2005 density-plume-generated advective deep-water renewal decreased and that this decrease fostered the development of anoxic conditions below 325 m in Lake Van. The discussion is based on the temporal changes in tracer distributions and suggests that the decrease in surface water density associated with lake level rise is the key mechanism responsible for the changes in mixing and oxic state in Lake Van.

5.1. Interpretation of θ and S with Respect to Deep-Water Exchange

[44] In lakes, dissolved substances and heat are transported vertically by vertical turbulent diffusion and by advective processes associated with density plumes. In deep lakes, convection during the cold season is usually not intense enough to cause vertical circulation and homogenization of dissolved substances and heat in the water column. Advective transport is typically dominated by density plumes propagating along the lake boundaries from the surface water regions down to the greatest depth [*Peeters and Kipfer*, 2009].

Table 4. Mean Averages and Standard Deviations of ^{3}H-^{3}He and Sulfur Hexafluoride (SF$_6$) Water Ages and Corresponding Residence Times for Different Depth Regions in Lake Van[a]

	^{3}H-^{3}He: 1990	^{3}H-^{3}He: 2005	SF$_6$: 2005
Mean water age Above 100 m	2 ± 2	5 ± 4	5 ± 3
Mean water age Below 325 m	10 ± 0.5	22 ± 3	22 ± 1
Mean residence time below 325 m	8 ± 2	17 ± 5	17 ± 3

[a] For ^{3}H-^{3}He water ages we used $(^3He/^4He)_{ter} = 5 \times 10^{-6}$ to obtain agreement between SF$_6$ and ^{3}H-^{3}He water ages.

[45] Vertical turbulent diffusion always causes heat to flow from high to low temperatures and, hence, leads to a gradual continuous warming of the cold deep water in temperature-stratified lakes. A decrease in temperature with depth, as is the case in Lake Van below 150 m, indicates that at least during some years, advective processes, transporting cold surface water down to the greatest depths, must have significantly contributed to deep-water renewal. Assuming steady-state conditions for the temperature stratification measured in Lake Van in 1990, the decrease in temperature with depth below 150 m can only be maintained if the heat flux by advective processes is sufficient to compensate the heat flux due to turbulent diffusion. Compared to 1990, temperatures in Lake Van have increased significantly at all depths below 150 m. The volume-weighted mean temperature increased from 3.24° to 3.34°C between 1990 and May 2005 in the water body below 200 m (Table 3). The warming of the deep water between 1990 and 2005 suggests that the downward transport of cold water by density plumes did not compensate for the heat flux by turbulent diffusion. Hence, the observed warming of deep water in Lake Van is consistent with the hypothesis of a reduced deep-water exchange by advective processes since 1990. An alternative explanation for the deep-water warming could be an increase in the transport of heat by turbulent mixing. However, increased turbulent diffusivities would lead to better oxygenation of the deep water and to faster removal of ^{3}He, both of which are contrary to the observation of a significant decrease in oxygen and an accumulation of ^{3}He in the deep water between 1990 and 2005. Alternatively, long-term warming of surface waters in response to rising air temperatures could have increased the temperature gradients and, thus, also the diffusive flux of heat. However, the consequences of surface warming for vertical heat transport are not easy to assess because the increase in stability associated with increased temperature gradients reduces the turbulence and thus leads to lower turbulent diffusivities. In comparison to surface warming as an explanation for the increase in heat content, the hypothesis of a decrease in deep-water advection has the advantage that it is consistent not only with deep-water warming, but also with the decrease in dissolved oxygen and the increase in ^{3}He concentrations.

[46] Deep-water advection usually is associated with density plumes and deep-water intrusions [*Peeters and Kipfer*, 2009]. In the following paragraph the potential mechanisms that could generate density plumes in Lake Van are discussed, and CTD profiles and thermistor data are analyzed with respect to density plumes and intrusions.

[47] As mentioned in section 1, neither freshwater inflows from rivers nor thermal bar and thermobaric effects can induce density plumes in Lake Van because of its high salinity (21 g kg^{-1}) and the associated low temperature at maximum density (T_{md} = −1.3°C). Differential cooling of the large shallow areas in the northeastern part of Lake Van may be a potential source of cold density plumes that could propagate to deep-water regions. However, in 2005 the salinity in the surface waters of the deep basin was at least 0.5 g kg^{-1}, and that in the shallow Erçis basin was 2.5 g kg^{-1}, lower than the salinity in the deep water, leading to chemical stabilization of the water column. Even if the surface water (S = 20.6 g kg^{-1}) is cooled down to T_{md} at the surface (θ = −1.3°C), the potential density of the deep water (S = 21.1 g kg^{-1} and θ = 3.3°C) is 0.3 kg m^{-3} higher than that of the cold surface water. A salinity of more than 20.95 g kg^{-1} is required so that the potential density of water with $\theta = -1.3$°C exceeds the ρ_{pot} = 1017.5 kg m^{-3} of the deep water in Lake Van. Hence, density plumes transporting cold water from the surface to the deep water become possible only if the salinity difference between surface and deep water is less than 0.15 g kg^{-1}. In all our data from 2005 and 2006 the lowest water temperature in the top 70 m was 3.5°C (in March 2006 at 25 m) and, thus, always above the deep-water temperature. This suggests that density plumes propagating down to the deep water of Lake Van would have required that the salinity in the surface water was higher than the S = 21.1 g kg^{-1} in the deep water.

[48] At open-water stations at a great depth the vertically averaged salinity in the top 70 m was about 20.9 g kg^{-1}, and about 0.2 g kg^{-1} lower than the deep-water salinities. In a vertically mixed surface layer, the salinity thus could be close to the salinity required for density driven deep-water mixing. Measurements from February 2006, conducted in the Van basin of Lake Van, confirm that during the cold season, the surface layer is mixed down to about 70 m and that the surface water has a salinity of 20.9 g kg^{-1}, which is about 0.2 g kg^{-1} lower than the salinity at the maximum depth of the profiles (140 m). However, in these profiles the surface water temperatures were above 4°C and the water column was stably stratified. Surface water with lower temperatures and thus higher densities may be generated in shallow-water areas by differential cooling. However, the shallow-water regions are often influenced by freshwater inflows and thus salinity in these regions may be lower than the salinity of the open water. This is especially the case for the water of the large shallow Ercis basin.

[49] Thermistor data from the mooring located at the entrance of the Erçis basin into the deep basin indicate that during some days in February and March, the temperatures in the top water layer were colder than the water at 70 m (Figure 4). However, the thermistor data do not show any signs of intrusions at depths below 70 m in 2005–2006. Intrusions could have been missed by the temperature measurements because of the large spacing of the moored thermistors. However, when surface water temperatures change, the density of downwelling water and, thus, the depth of the resulting intrusions also change, and one may expect that the intrusions then could be detected at the depth of the thermistors. Furthermore, we carried out high-resolution CTD measurements in 2005 and 2006 at different positions in the lake and did not find remnants of cold-water intrusions below 70 m, except in one region of the lake. These few intrusions with a lower temperature than the open lake water were all associated with lower oxygen concentrations and higher salinities. They were observed in some CTD profiles in Tatvan Bay, slightly above the lake bottom, which was at depths of between 120 and 240 m. The characteristic properties of the intrusive water suggest that it was either ground water or water from the margins of the lake that lost oxygen in contact with the sediments as it moved downward along the slope. Groundwater intrusions have been reported earlier to infiltrate the lake at different places at the lake shore of Lake Van, for example, Tatvan Bay [*Gessner*, 1957; *Kempe et al.*, 1991]. However, we did not find any indication of density plumes bringing oxygen-rich cold surface water to a depth greater

than 70 m in our CTD profiles or in our mooring data for 2005–2006.

[50] The previous discussion suggests that density stratification due to salinity gradients most likely prevented deep-water oxygenation by density plumes in 2005 and 2006. But also in 1990, conditions for deep-water mixing were similar to those in 2005. In June 1990 at the deepest station, the mean salinity in the top 70 m and the difference in the salinity of the surface water versus the deep water were essentially the same as in 2005, assuming that our calibration of the conductivity sensor also applies to the sensor employed in 1990. Note also that the lake level was essentially the same in June 1990 and May 2005. The salinity profiles from these two years suggest that differential cooling alone most likely was not sufficient to cause density plumes in 2005 or in 1990 and that an increase in salinity would have been required to cause convective mixing.

[51] A lake level change can have a significant effect on the salt budget of the surface layer in saline lakes. Assuming that salt can be treated as a conservative tracer, a level increase of 1 m in Lake Van implies a decrease in the overall salt budget that corresponds to a decrease of 0.39 g kg^{-1} in the mean salinity of the top 70 m. In winter 1988 the level of Lake Van was about 1 m lower than in June 1990. Hence the preceding estimate suggests that the mean salinity in the top 70 m may have been about 0.4 g kg^{-1} higher in winter 1988 than in June 1990. Thus, at the reduced lake level in 1988, salinity in the surface layer could have been sufficient to allow the generation of density plumes and convective mixing. Note, however, that the estimated change in surface water salinity applies to the entire water layer above 70 m and, thus, also includes, for example, the Ercis basin. Horizontal mixing of low-salinity water from the Ercis basin with the surface water in the central basin reduces salinity in the open water, and the change in salinity due to the lake level change may thus not have been as large as suggested by the preceding calculation. The lake level decrease of about 0.4 m from May 2005 to February 2006 did not result in a clear increase in the mean salinity of the top 70 m at the measuring sites. Nevertheless, the decrease in the salt budget associated with the observed increase in lake level by 1 m between 1988 and 1990, and by another meter up till 1999, is sufficiently large to have an effect on the generation of density plumes and convective mixing.

[52] Vertical mixing by turbulent diffusion can be quantified based on the vertical eddy diffusion coefficient K_z, which was estimated by using the discrete heat budget method [*Powell and Jassby*, 1974] and assuming a geothermal heat flux of 0.1 Wm^{-2} [*Wüest et al.*, 1992]. K_z calculated from CTD profiles measured in May 2005 and in September 2005 decreased from about 8×10^{-5} m^2 s^{-1} at 100 m to about 2×10^{-5} m^2 s^{-1} at 250 m. These values are of the order of magnitude typical for deep water in lakes and are, for example, smaller than those obtained at 150 m in the meromictic Lake Lugano [*Aeschbach-Hertig et al.*, 2007]. Because density plumes propagating to the deep water cannot occur during the summer period when the surface water temperatures are high, the previously calculated K_z values are assumed to be representative for turbulent diffusive mixing in Lake Van. The estimated K_z varied by less than 50%, independent of whether the calculation was based on CTD profiles from May and September 2005, from May 2005 and July 2006, or from September 2005 and July 2006. This supports that a K_z of the order 5×10^{-5} m^2 s^{-1} is typical for the years 2005 and 2006. Below 250 m the increase in heat content was about 3 times larger than that expected from geothermal heating, and below 100 m geothermal heating accounted for less than one sixth of the increase in heat content. Note that between September 2005 and July 2006 the heat content below 100 m and below 250 m, respectively, increased at rates similar to those during summer 2005. If advective transport of cold water to depths below 100 m occurred at all during the cold season in 2005–2006, it apparently was not sufficient to compensate for the positive heat flux to the deep water by turbulent diffusion.

[53] Temperatures, measured nearly continuously with thermistors in the deep water between July 2006 and January 2008, increased linearly with time at a rate of 0.011°C a^{-1} at 430 m and 0.016°C a^{-1} at 400 m water depth. According to the thermistor data, sudden temperature changes indicating intrusions of cold water down to the greatest depths did not occur during the time period of our field campaigns. However, before 1990, advective transport of cold water down to the deepest water layers must have occurred because the decrease in temperature with depth and the low temperatures in the deep water observed in the temperature profiles require, at least sporadically, advective transport of cold water. Hence, the findings from salinity and temperature data support the hypothesis that advective transport was more intense in the time period before the lake level rise.

5.2. The Change in Oxygen Concentration Between 1990 and 2005

[54] Between 1990 and 2005 oxygen concentrations below 100 m decreased significantly, leading to anoxic conditions below 325 m in 2005. Deep-water oxygen concentrations result from a balance of oxygen consumption and oxygen renewal. Steady oxic conditions can only be maintained if the oxygen consumption rate is compensated by the gradient in the oxygen flux. Assuming a constant oxygen consumption rate, the decrease in the deep-water oxygen concentration suggests that, compared to the years before 1990, the vertical flux of oxygen associated with deep-water renewal was significantly reduced between 1990 and 2005.

[55] The oxygen consumption rate can be obtained by linear regression of the oxygen deficit (apparent oxygen utilization) versus the SF_6 water age [*Jenkins*, 1977; *Kipfer et al.*, 2002] and turns out to be 0.5 ± 0.1 g m^{-3} a^{-1} in Lake Van considering the depth range between 50 and 325 m. The estimate of the oxygen consumption rate assumes that the consumption rate is constant over time. This assumption is supported by the data because the oxygen deficit is highly correlated with the SF_6 water age (Figure 7; correlation coefficient $r = 0.95$, $p < 10^{-4}$; $n = 9$) and 90% of the variance of the oxygen deficit is explained by the linear regression model between the oxygen deficit and the SF_6 water age. Furthermore, the residues of the linear regression are not correlated with SF_6 water age ($p = 1$; $n = 9$).

[56] From the oxygen profile and the turbulent diffusion coefficients determined, the oxygen flux due to turbulent diffusion at 200 m can be estimated to be 3×10^{10} g a^{-1} (using $K_z = 5 \times 10^{-5}$ m^2 s^{-1}) in 2005. In 1990 the vertical oxygen gradient at 200 m was a factor of ~2 smaller than in

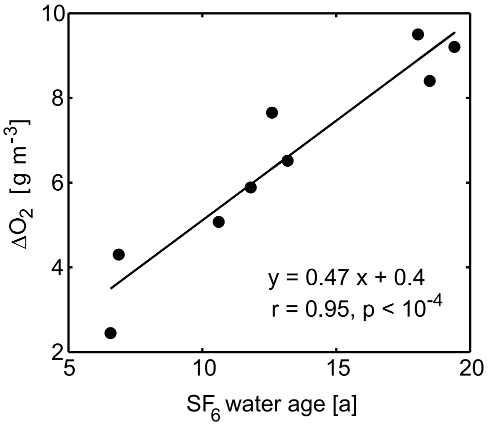

Figure 7. Correlation between oxygen deficit and SF_6 water age at between 50 and 325 m in 2005. The oxygen consumption rate in the water column corresponds to the slope of the regression line.

2005, suggesting that the oxygen flux due to turbulent diffusion in 1990 was smaller than in 2005. Even if the turbulent diffusivity in 1990 was 1×10^{-4} m^2 s^{-1}, as suggested by *Wüest et al.* [1992], the oxygen flux due to diffusive transport was ~3×10^{10} g a^{-1} in 1990 and, thus, about the same as in 2005. Assuming that oxygen concentrations were at steady state in 1990 and that the oxygen consumption rate is 0.5 ± 0.1 g m^{-3} a^{-1}, oxygen depletion below 200 m was about 8×10^{10} g a^{-1}. With a diffusive oxygen flux of 3×10^{10} g a^{-1} at 200 m, the oxygen flux due to advective processes to depths below 200 m must have been 5×10^{10} g a^{-1} to compensate oxygen loss. Hence, in 1990 advective processes must have contributed substantially to the oxygen transport into the deep water. Between 1990 and 2005, the total amount of oxygen below a depth of 200 m decreased by 3×10^{11} g, from about 4×10^{11} to about 1×10^{11} g (Table 3). Assuming that oxygen depletion and oxygen flux by turbulent diffusion below 200 m remained unchanged and that advective transport to depths below 200 m ceased in 1990, the net annual oxygen loss would have been 5×10^{10} g a^{-1}. Then the reduction in the total amount of oxygen below 200 m between 1990 and 2005 would have been reached within about 6 years. Hence, under the preceding assumptions, the observed decrease in oxygen below 200 m between 1990 and 2005 is consistent with a substantial reduction in advective transport, by about 40%. Note, however, that this estimate assumes a constant oxygen depletion rate in the water below 200 m, which may not be adequate after the deep water has become partially anoxic. Nevertheless, the oxygen data support the hypothesis of a strong reduction of advective deep-water renewal.

5.3. ^{3}H and ^{3}He Balance

[57] The volume-weighted mean ^3H concentration (Table 3) below 200 m decreased by 12.2 TU between 1990 and 2005, which agrees well with the 11.7 TU expected from radioactive decay of ^3H. Between 1990 and 2005 the decay of ^3H produced 2.9×10^{14} cm^3 STP g^{-1} ^3He in the deep water of Lake Van. The ^3He produced by ^3H decay together with ^3He from the influx of the terrigenic component apparently has accumulated below 200 m since 1990 and was not completely removed by mixing and subsequent gas exchange with the atmosphere. Because ^3He in the deep water increased by 1.8×10^{14} cm^3 STP g^{-1}, that is, only by about two thirds of the ^3He produced by ^3H decay, a significant part of the ^3He must have been vertically transported by mixing. The vertical gradients of ^3He and the turbulent diffusivities determined here imply that some ^3He must be have been transported vertically by turbulent diffusion. Nevertheless, ^3He accumulated in the deep water, suggesting that overall deep-water renewal has been reduced after 1990.

5.4. Residence Times

[58] The residence time of 17 years in the anoxic deep water in 2005 derived from SF_6 water ages supports the hypothesis of reduced deep-water renewal since the beginning of the lake level rise in 1988. If the residence time of the deep water was 1–2 years in 1989–1990, as estimated by *Kipfer et al.* [1994], the residence time of 17 years, measured in 2005, suggests that no mixing has occurred since 1989/1990. However, the rising SF_6 concentrations in the atmosphere must have resulted in increasing concentrations in the surface waters, leading to an increase in the vertical SF_6 gradient. Hence, SF_6 must have been transported downward by turbulent diffusion, thus reducing residence times in the deep water. Most likely, *Kipfer et al.* [1994] underestimated the residence times in 1989/1990 because their estimates were based on a rather high $(^3He/^4He)_{ter} = 1 \times 10^{-5}$. If ^3H-^3He water age is based on $(^3He/^4He)_{ter} = 5 \times 10^{-6}$, the deep-water residence time obtained from ^3H-^3He water ages for 1990 is about 8 years, suggesting deep-water renewal of 12.5% per year in the case of continuous renewal or stagnant conditions over 8 years in the case of complete mixing, followed by a period without deep-water exchange. This deep-water renewal rate of 8 years is consistent with the findings of *Reimer et al.* [2009], who concluded on the basis of phosphate and dissolved oxygen data that in 1990 the deep water was not mixed for at least 7 years. According to ^3H-^3He water ages based on $(^3He/^4He)_{ter} = 5 \times 10^{-6}$, the deep-water residence time increased from 8 ± 2 years in 1990 to 17 ± 5 years in 2005 (Table 4), suggesting that deep-water renewal has decreased substantially since 1990. The suggested 9 year increase in deep-water residence within a 15 year time period implies that some vertical deep-water exchange has occurred since 1990 and, thus, allows for diffusive transport of transient tracers and heat and is consistent with the changes in concentrations of ^3He and dissolved oxygen between 1990 and 2005.

5.5. Reduced Deep-Water Renewal and Lake Level Change

[59] The tracer data, in particular, the decrease in dissolved oxygen together with the increase in ^3He concentrations in the deep water, below 100 m, between 1989/1990 and 2005/2006 indicate that deep-water renewal in Lake Van was reduced during this time period. The preceding arguments suggest that, especially, advective deep-water transport by density plumes was less intense between 1989 and 2006 than prior to 1989. The probability for the generation of density plumes is reduced when freshwater inflows into a saline lake increase because the freshwater input leads to a lower water density in the surface water. In

addition, the increased density stratification is expected to suppress turbulence and thus result in lower turbulent diffusivities. Hence, the preceding discussion suggests that the reduction in deep-water renewal in Lake Van between 1989 and 2006 was a consequence of the freshwater inflows associated with the lake level increase between 1989 and 1995.

6. Conclusions

[60] The observations from Lake Van suggest that in large saline lakes, even small changes in the hydrological regime can have a large impact on deep-water renewal. The lake level increase of 2 m reduced deep-water exchange in Lake Van sufficiently that a more than 100 m thick deep-water body became anoxic. Thus, small changes in the hydrological regime can also have severe consequences for biogeochemical conditions in deep saline lakes. Furthermore, the consequences from a disturbance of the system may prevail for substantially longer than the disturbance itself, that is, the anoxic conditions in the deep water were still present 10 years after the maximum lake level was reached and 3 years after the level had returned to the level of 1989. Hence, regularly recurring small level rises, of a few meters, may substantially affect deep-water conditions over very long periods of time. Because a lake level rise of 2 m had already strongly reduced deep-water renewal and caused anoxic conditions below 325 m, substantially larger lake level increases or periods of lake fluctuations similar to those between 1990 and 2007, but recurring over extended periods of time [see *Landmann et al.*, 1996; *Wick et al.*, 2003], most likely have severe consequences for the entire ecosystem. These should be reflected in sediment records and must be taken into account when interpreting lakeborne proxies.

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