

# Contribution of Solutes to Density Stratification in a Meromictic Lake (Waldsee/Germany)

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Received: 25 September 2011 / Accepted: 3 April 2012 / Published online: 28 April 2012  
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**Abstract** Density differences are the key parameter for stratification stability. We used data from the iron-meromictic Waldsee, Germany, a lignite mine pit lake, to quantify the contribution of single solutes to water density and analyzed the density gradient. Iron meromictic lakes maintain their density gradient through chemical reactions. Hence, quantifying the contributions of separate solutes is essential for understanding the entire process. Based on solute concentrations and literature values of partial molal volumes, substance specific density contributions were quantitatively evaluated. Then, by direct measurements of the density of IHSS Waskish peat fulvic acid, we quantified the density contribution of dissolved organic carbon (DOC). While several solutes contributed to the density throughout the water column, only those substances that occurred at higher concentrations in the anoxic monimolimnion than in the oxic mixolimnion were crucial to sustaining the density difference between the two layers. In Waldsee, the density difference between monimolimnion and mixolimnion was attributed to dissolved  $\text{Fe}^{2+}$  (0.23 g/L, resulting in a 45 % of the density difference due to solutes) and to the carbonate system ( $\text{HCO}_3^-$ , about 0.16 g/L and  $\text{CO}_2$ , 0.03 g/L) while  $\text{Ca}^{2+}$  and DOC delivered only a small contribution. In summer, total density differences were dominated by temperature differences; during winter, solutes sustained meromixis. Finally, we

present a complete list of specific density fractions for basically all of the density-relevant substances in fresh waters.

**Keywords** Density stratification · Iron cycle · Meromixis · Water density calculation

## Introduction

Water density is an important physical variable that depends on temperature, chemical composition, and pressure. Density differences determine the maintenance of stratification, cause mixing processes, drive water currents, and thereby distribute oxygen and nutrients in the water column. Hence, they are one of the most important determinants of the ecological features of water bodies (Wetzel 2001).

Meromictic lakes show permanent density stratification. They have a denser deep water body (the monimolimnion), which is separated from the surface water layer (the mixolimnion) by a pycnocline—a zone with an abrupt density increase. The entire water body does not seasonally overturn. Causes for the development of meromixis are manifold (Boehrer and Schultze 2008; Hutchinson 1957) and range from external causes, such as the inflow of higher mineralized groundwater, e.g. pit lakes Merseburg Ost 1a and 1b, Germany (Böhrer et al. 1998; Heidenreich et al. 1999; von Rohden and Ilmberger 2001), to lake-internal biogeochemical reactions. For example, Lake Gråvtjern and Lake Ljøgodttjern (Norway; Hongve 1980) are characterized by high  $\text{Fe}^{2+}$  concentrations, while Lake Vesle Bakketjern (Norway) is permanently stratified due to high concentrations of dissolved organic matter and  $\text{CO}_2$  (Hongve 1980).

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Water density can be measured or calculated. Direct field measurements of density are not very accurate (Gräfe et al. 2002), so indirect methods based on temperature and salinity have been developed, e.g. an equation by Chen and Millero (1986), which is valid for freshwater with salinities less than 0.6 practical salinity units (1 psu is approximately 0.1 ‰ salinity). Lake-specific coefficients can be obtained and a density equation can be set up using the conductivity and density measurements (e.g. Boehrer et al. 2009; Bühner and Ambühl 1975; Jellison and Melack 1993; Karakas et al. 2003).

In many cases, chemical analyses of lake waters are available. Water density calculations based on chemical compositions must consider that the density contribution of any given molecule depends not just on its molar mass, but also on its effect on water volume (e.g. Boehrer et al. 2010; Millero 2001). Also, solutes (e.g. gases) that do not contribute to conductivity must be included in the calculations. Wüest et al. (1996), who calculated water density in Lake Malawi based on solutes, emphasize the importance of dissolved gases to lake stability.

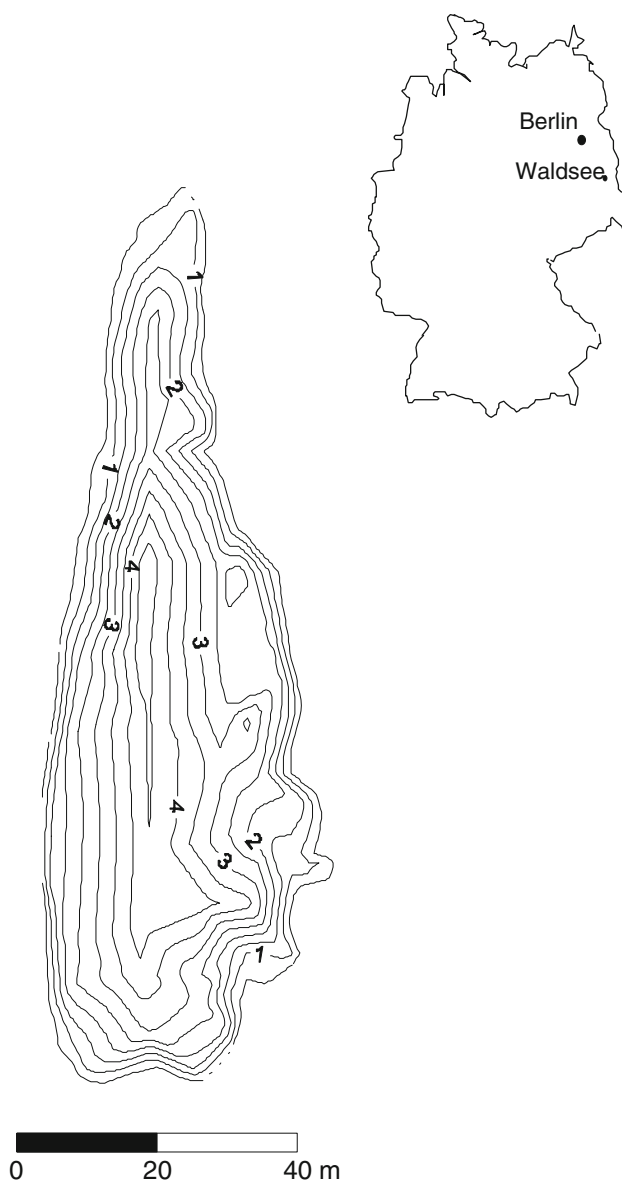
In contrast to Wüest et al. (1996), who stoichiometrically combined ions to salts, we quantified the density contribution for each solute separately to quantify its portion in sustaining meromixis.

Using the example of the meromictic Waldsee in Germany, we quantified to what extent solutes contribute to water density in the different water layers. Furthermore, we identified the crucial chemical constituents that sustained the density gradients between mixolimnion and monimolimnion and documented seasonal variations. Finally, we list specific density fractions of basically all density relevant substances in fresh waters to allow others to easily use this approach.

## Methods and Characterization of the Study Site

### Study Site

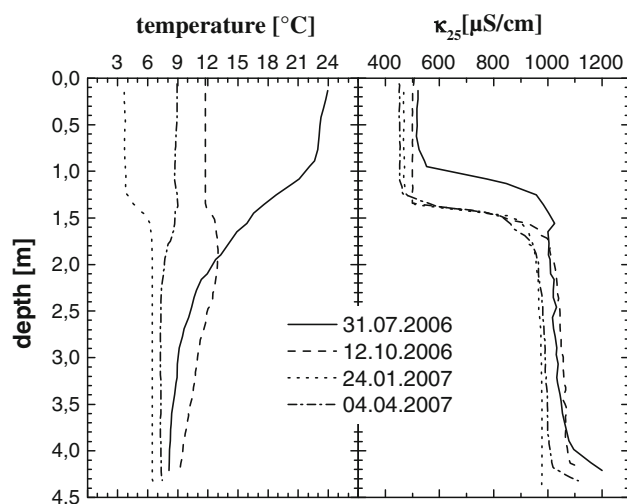
Waldsee is a small (volume: 6,542 m<sup>3</sup>, surface area: 2,387 m<sup>2</sup>) and relatively shallow (maximum depth: 4.7 m, mean depth: 2.1 m) pit lake located in the lignite mining district of Lusatia, ca. 120 km southeast of Berlin (coordinates: 51°37′14.1″N, 14°34′16.7″E) (Fig. 1). The lake is protected from strong winds by the surrounding forest and receives virtually all of its recharge by groundwater (Seebach et al. 2008; von Rohden et al. 2009). The geological setting of the surrounding area is complex (e.g. Seebach et al. 2008; von Rohden et al. 2009). Its monimolimnion volume is exchanged almost once a year (von Rohden et al. 2009).



**Fig. 1** Bathymetric map of Waldsee

### Lake Stratification

The mixolimnion comprised a water layer of only 1–1.5 m and did not thermally stratify during summer (Fig. 2). The pycnocline, which was marked by a steep gradient in conductance ( $\kappa_{25}$ ), was closest to the lake surface in July 2006 and deepest in November 2006. Its lowering was the result of nocturnal mixolimnetic thermal convection during the warm season (von Rohden et al. 2009). Heat input caused a temperature increase in the monimolimnion during summer. As a consequence of the faster cooling of the mixolimnion in autumn, instabilities were generated below the pycnocline, leading to an internal mixing of the monimolimnion, as shown by equal temperature and



**Fig. 2** Temperature and electric conductance ( $\kappa_{25}$ ) profiles of Waldsee on specific dates from summer 2006 until spring 2007. Electric conductance was calculated according to Boehrer et al. (2009)

conductance (Fig. 2) (see also Boehrer et al. 2009; von Rohden et al. 2009).

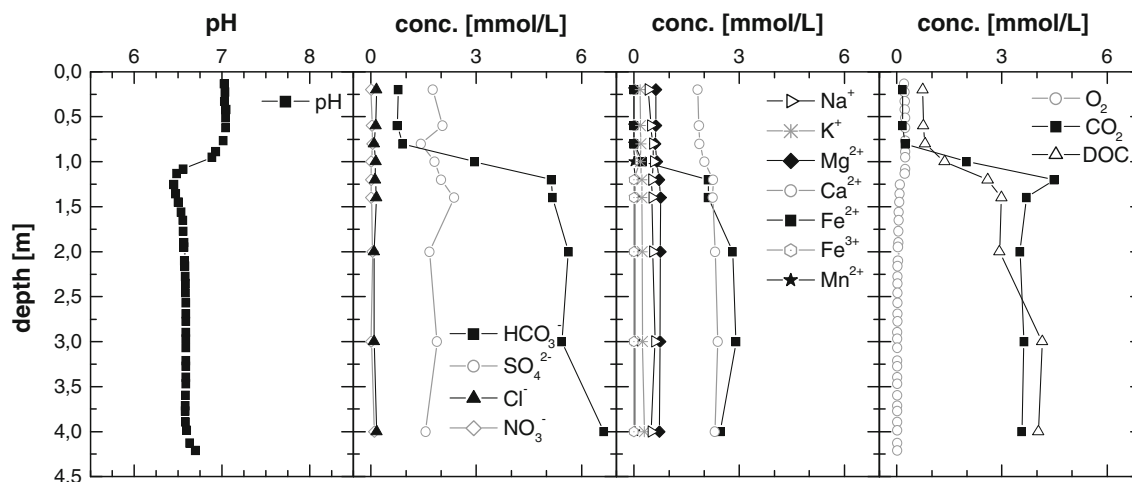
#### Analytical Methods

Density calculations of Waldsee water were based on chemical analyses and *in-situ* measurements from 2006 and 2007. Temperature, *in-situ* conductivity, and oxygen concentrations were obtained from a multiparameter probe (Ocean Seven, Idronaut, Italy). Samples were taken with a submerged pump at the deepest part of the lake, filtered through 0.45  $\mu\text{m}$  cellulose-acetate filters, and analyzed by ion chromatography for  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , and  $\text{NO}_3^-$ , atomic

absorption spectrometry for  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mn}^{2+}$ , and Fe, and in addition photometry for  $\text{Fe}^{2+}$ . DOC (dissolved organic carbon) concentrations were measured with the TOC-analyzer 5000 (Shimadzu, Japan).

#### Chemical Characterization

The pH of Waldsee water lay in the neutral range and was slightly higher in the surface water than in the monimolimnion (Fig. 3). The mixolimnion mainly contained the solutes  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$ . In July 2006, their mean concentrations were 1.8 and 1.9 mmol/L, respectively. Concentrations of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Cl}^-$  were one order of magnitude lower;  $\text{NO}_3^-$  concentrations were two orders of magnitude lower. In the pycnocline, the concentrations of most solutes increased, except for  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , and  $\text{NO}_3^-$ . Their mean monimolimnetic concentrations were similar or slightly lower than in the mixolimnion. The deep water body composition was dominated by high  $\text{Fe}^{2+}$  concentrations, about 2.6 mmol/L, which corresponded to an enrichment factor of nearly 9,000 compared with the mixolimnion water.  $\text{Mn}^{2+}$  concentrations increased in the water column by a factor of about five and reached values up to 0.02 mmol/L. The accumulation factor for all other cations ranged from 1.2 to 1.5 in the monimolimnion, except for  $\text{Fe}^{3+}$ .  $\text{HCO}_3^-$  and  $\text{CO}_2$  concentrations were evaluated from pH and TIC (total inorganic carbon) concentrations using the geochemical model Phreeqc (Parkhurst and Appelo 1999). Their concentration increased from 0.92 to 11.2 mmol/L with depth.  $\text{CO}_2$  was the most common gas (mean: 3.6 mmol/L) and  $\text{HCO}_3^-$  was the predominant anion (mean: 5.7 mmol/L) in the monimolimnion. Due to the exclusion of the monimolimnion from gas exchange with the atmosphere, oxygen was only



**Fig. 3** Concentration gradients in Waldsee on 31 July 2006, based on probe profiles of pH and  $\text{O}_2$  concentration and results of chemical analyses from definite sampling depths

present in the surface water ( $\approx 0.2$  mmol/L) and decreased to zero in the pycnocline.

### Specific Density Contribution of Solutes

Lake water represents an aqueous solution of numerous substances. Therefore, calculations of density and concentrations are complex and are usually not performed extensively in limnological studies. Hence, the mathematical derivation is given here in detail. We consider a solution of  $b_i$  moles of several substances (indexed  $i$ ) of the molecular mass  $M_i$  in a water volume with the mass  $m_W = 1$  kg (i.e. molal units). The mass of the solution is simply the sum of the contributions:

$$m = m_W + \sum b_i M_i \quad (1)$$

However, dissolved substances in the water also change the volume. For most substances, the volume becomes larger; but there are a few exceptions, where the volume becomes smaller. In total, the volume of this solution is given by the volume of the water  $V_W$  and the specific contribution of the substances, called partial molal volumes  $V_i$ :

$$V = V_W + \sum b_i V_i \quad (2)$$

For each solute  $n = i$  in the solution, we have  $b_n$  moles in a solution of the volume  $V$ :

$$c_n = \frac{b_n}{V_W + \sum b_i V_i} \quad (3)$$

For our numerical evaluation, we need to derive molal ( $b_n$ ) units from measured concentrations ( $c_n$ ) from the field samples:

$$b_n = c_n \cdot (V_W + \sum b_i V_i) \quad (4)$$

In this step, we require molal concentrations of all (other) solutes, which are only available in molar concentrations. Hence, we approximate the amount of substances in the sum by  $b_i \approx c_i \cdot V_W$ . Inserted in Eq. 4, this yields a first order approximation of  $b_n$ , which can be used again to get a better approximation. This iterative method converges very fast. The high-order results showed that the final result was approximated in the first calculation step sufficiently well.

Density  $\rho$  is calculated from the mass of the solution divided by its volume:

$$\rho = \frac{m_W + \sum b_i M_i}{V_W + \sum b_i V_i} \quad (5)$$

Our interest is focused on the density contribution  $\Delta\rho_n$  of each component  $n$  in the solution. This is numerically evaluated by a derivation by parts and referring to Eq. 5:

$$\begin{aligned} \Delta\rho_n &= b_n \cdot \frac{\partial\rho}{\partial b_n} = b_n \cdot \frac{\partial}{\partial b_n} \cdot \left( \frac{m_W + \sum b_i M_i}{V_W + \sum b_i V_i} \right) \\ &= b_n \cdot \frac{M_n - V_n \cdot \rho}{V_W + \sum b_i V_i} \end{aligned} \quad (6)$$

In Eq. 5, when referring to water in which several different solutes are dissolved at any concentration, we now focus on dilute conditions, which is appropriate for Waldsee. Under dilute conditions,  $\sum b_i V_i < V_W$ , so it can be neglected. For an unspecific mass of water,  $b_n$  is replaced by  $b_n^*$  moles per kg of water (molal units), and  $V_W$  is replaced by the specific volume of water  $V_W^*$ . Under dilute conditions, we can calculate the specific contribution of a solute to water density, which is called the density contribution coefficient  $\beta_n$ .

$$\beta_n = \frac{\Delta\rho_n}{b_n^*} = \frac{M_n - V_n \cdot \rho}{V_W^*} \quad (7)$$

The complete set of partial molal volumes (Table 1) that we require for Waldsee conditions is only available for a temperature of 25 °C. The specific volume of pure water of about  $V_W = 1.0029$  L/kg was evaluated from its density at 25 °C (Lide 2008). A list of the density contribution coefficients ( $\beta_n$ ) for the most important solutes required in limnology is presented in Table 1.

If the molecular structure of a substance is unknown, as it is for the bulk parameter DOC, giving concentrations in mass per volume may be the more appropriate approach. We define

$$\tilde{c}_n = M_n c_n = \frac{M_n b_n}{V_W + \sum b_i V_i} \quad (8)$$

which relates the mass of dissolved substance to the volume of the solution, and hence has the unit of density. As a consequence, Eq. 6 becomes:

$$\Delta\rho_n = b_n \cdot \frac{\partial\rho}{\partial b_n} = \tilde{c}_n \cdot \frac{\partial\rho}{\partial \tilde{c}_n} = \tilde{c}_n \cdot \gamma_n \quad (9)$$

where the specific density fraction  $\gamma_n = \frac{V_W + \sum b_i V_i}{M_n} \beta_n \approx \frac{V_W}{M_n} \beta_n$  relates the gained density in g/L to the concentration in g/L, assuming dilute conditions, and hence,  $\gamma_n$  is dimensionless. The respective values can be supplied for the discussed ion species (see Table 1). In general, gases have the smallest coefficients, even below 0, while the density effect increases with the charge of the ion, beyond the factor of 3 for  $\text{Al}^{3+}$ .  $\text{H}^+$  is an exception due to its small molar mass. As a consequence, it possesses the greatest specific density fraction ( $>5$ ).

We did not know of any publication that related the concentrations of DOC or dissolved humic substances to density. As a consequence, we performed laboratory measurements of our own to fill this gap. We dissolved 0.00980 g of IHSS Waskish peat fulvic acid in 0.02 L of

**Table 1** Molar mass (g/mol), partial molal volumes (L/mol), specific expansion coefficient,  $\beta_n$ , (g kg/(mol L)), specific density fraction  $\gamma_n$  of ions and gases, and the specific density fraction for DOC

Solute	Molar mass ( $M_i$ )	Molal volume ( $V_i$ )	Density contribution coefficient ( $\beta_n$ )	Specific density fraction, $\gamma_n$
H <sup>+</sup>	1.008	−0.0045	5.48	5.451
Na <sup>+</sup>	22.99	−0.0057	28.59	1.247
K <sup>+</sup>	39.1	0.0045	34.63	0.885
Mg <sup>2+</sup>	24.31	−0.0301	54.16	2.235
Ca <sup>2+</sup>	40.08	−0.0269	66.70	1.669
NH <sub>4</sub> <sup>+</sup>	18.042	0.0134	4.67	0.259
Fe <sup>2+</sup>	55.85	−0.0351	90.58	1.627
Fe <sup>3+</sup>	55.85	−0.0470	102.41	1.839
Mn <sup>2+</sup>	54.94	−0.0227	77.34	1.412
Al <sup>3+</sup>	26.98	−0.055	81.58	3.033
OH <sup>−</sup>	17.007	0.0005	16.46	0.971
HCO <sub>3</sub> <sup>−</sup>	61.015	0.0274	33.60	0.552
CO <sub>3</sub> <sup>2−</sup>	60.008	0.0049	54.94	0.919
SO <sub>4</sub> <sup>2−</sup>	96.066	0.0229	73.30	0.762
Cl <sup>−</sup>	35.45	0.0223	13.18	0.373
NO <sub>3</sub> <sup>−</sup>	62.007	0.0335	28.52	0.461
NO <sub>2</sub> <sup>−</sup>	46.008	0.0295	16.55	0.361
HPO <sub>4</sub> <sup>2−</sup>	95.974	0.017	78.79	0.823
Si(OH) <sub>4</sub>	96.114	0.0615	34.69	0.362
CO <sub>2</sub>	44.008	0.0348	9.28	0.212
O <sub>2</sub>	31.998	0.0310	1.09	0.034
CH <sub>4</sub>	16.043	0.0374	−21.18	−1.324
N <sub>2</sub>	28.02	0.0333	−5.17	−0.185
DOC	—	—	—	0.667

Data for partial molar volumes at 25 °C for ions were taken from Millero (1969), for gases from Enns et al. (1965) and for Si(OH)<sub>4</sub> from Duedall et al. (1976). Density contribution coefficient  $\beta_n$  and specific density fraction  $\gamma_n$  were calculated according to equation (8 or 10) for dilute conditions and 25 °C. The specific density fraction for DOC [(g/L)/(gDOC/L)] (in the narrower sense, IHSS Waskish peat fulvic acid washid) was evaluated from own measurements (see “Appendix”)

pure water and measured its density using a PAAR DSA 5000 (Austria) densitometer. According to IHSS (2008), carbon contributes 53.17 % of the mass, yielding a concentration of 0.261 g/L DOC in the solution. For more detail on this measurement, see “Appendix”, which is provided in the electronic version of this paper and can be downloaded for free by all subscribers. At 24.995 °C, a density difference of 0.174 g/L was found, compared with pure water measured at the same temperature using the same equipment. In conclusion, a density difference of 0.667 [0.174 (g/L)/0.261 (g/L DOC)] was attributed to the IHSS Waskish peat fulvic acid, representing the specific density fraction,  $\gamma$ , for DOC. Missing better data for the density contribution of DOC in Waldsee, we used this coefficient, although fully aware that a more reliable number would require much more detailed investigation of DOC and the density of natural waters.

## Results of the Density Calculations for Waldsee

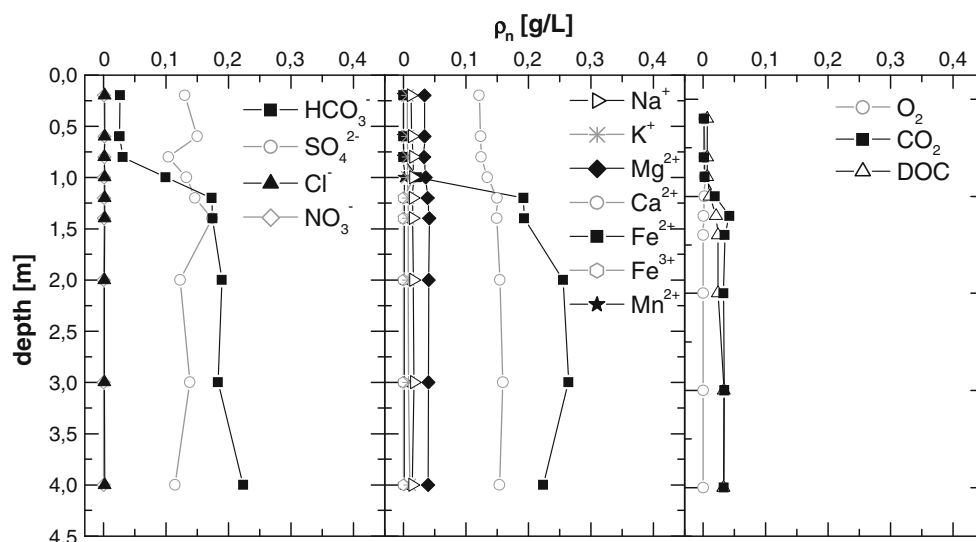
We applied Eq. 6 to our measurements of solutes in Waldsee (Fig. 3). We found that only a few solutes were consistently relevant to water density: Fe<sup>2+</sup> (up to 0.26 g/L)

and HCO<sub>3</sub><sup>−</sup> (up to 0.22 g/L), Ca<sup>2+</sup> (up to 0.17 g/L), and SO<sub>4</sub><sup>2−</sup> (0.13 g/L) contributed to density over the entire water depth. Other solutes, Mg<sup>2+</sup>, CO<sub>2</sub> or DOC, and other ions were much less significant to density (Fig. 4; Table 2).

The density difference between mixolimnion and monimolimnion was sustained by the solutes that were not equally distributed over the water column, but showed a concentration gradient across the chemocline. Consequently, most of the density difference between mixolimnion and monimolimnion was contributed by Fe<sup>2+</sup> (0.23 g/L) and HCO<sub>3</sub><sup>−</sup> (0.16 g/L). Smaller density gradients could be attributed to CO<sub>2</sub> (0.03 g/L), Ca<sup>2+</sup> (0.04 g/L), and DOC (0.03 g/L), as shown in Fig. 4 and Table 2. We were aware that the chemical composition of the dissolved organic matter in Waldsee might not concur with the chemical composition of IHSS Waskish peat fulvic acid. A possible large relative error resulting from such differences would not change the general result. The contributions of other solutes to the density gradient (e.g. Mg<sup>2+</sup>) were marginal. This was even true for SO<sub>4</sub><sup>2−</sup>, despite its absolute relevance to density over the entire water column (Table 2).

Density stratification was dominated by temperature gradients in July 2006 and solely maintained by solutes in January 2007. Density differences were 2.80 (July) and

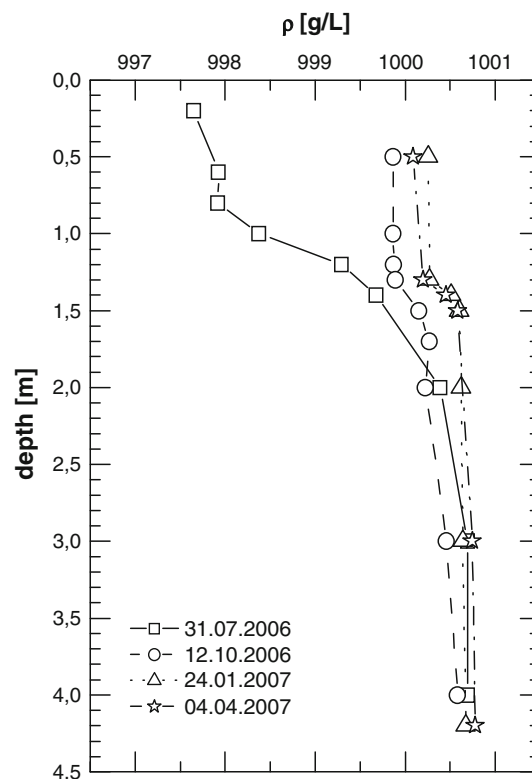
**Fig. 4** Density contribution of anions, cations, and gases in Waldsee on 31 July 2006



**Table 2** Mean density contribution of solutes in mixolimnion and monimolimnion and their contribution to the chemical density increase in the monimolimnion of Waldsee on 31 July 2006

Solute	Density contribution ( $\rho_n$ ) (%)		Contribution to chemical density difference mixolimnion–monimolimnion (%)
	Mixolimnion	Monimolimnion	
Na <sup>+</sup>	3.56	1.81	0.69
K <sup>+</sup>	1.76	0.99	0.50
Mg <sup>2+</sup>	9.41	4.59	1.55
Ca <sup>2+</sup>	32.59	17.80	8.33
Fe <sup>2+</sup>	0.00	27.45	44.58
Fe <sup>3+</sup>	0.13	0	−0.08
Mn <sup>2+</sup>	0.07	0.17	0.23
HCO <sub>3</sub> <sup>−</sup>	8.33	22.28	30.83
SO <sub>4</sub> <sup>2−</sup>	40.71	15.58	−0.10
Cl <sup>−</sup>	0.60	0.24	0.02
NO <sub>3</sub> <sup>−</sup>	0.13	0.04	−0.03
CO <sub>2</sub>	0.86	3.87	5.81
O <sub>2</sub>	0.81	0	−0.50
DOC	1.70	4.31	6.68

0.42 g/L (January), respectively (Fig. 5), and therefore at least seven times lower than in Mono Lake (Jellison and Melack 1993). Meromixis can occur at even lower density differences, as shown by Brunskill and Ludlam (1969), who approximated a density difference of about  $0.6 \cdot 10^{-3}$  g/cm<sup>3</sup> for Green Lake (NY). For dimictic Lake Onondaga, where the stratification is also influenced by a higher concentration of solutes in the deep water layer, Eiffler et al. (1986) evaluated a density difference of about 0.003 g/L, including a salinity component of about 41 % during the summer months.



**Fig. 5** Calculated density profiles for Waldsee on specific dates from summer 2006 until spring 2007. The calculations are based on data from *in-situ* temperature measurements and chemical density calculations

In Waldsee, density stratification caused by solutes varied little ( $0.51 \pm 0.04$  g/L) throughout the year. Hence, solutes contributed 18 % to density stratification in July 2006 and 90 % in October 2006. In January 2007, solutes contributed 110 % to the entire density gradient, balancing



the adverse density gradient due to low mixolimnion temperatures (Fig. 2).

Water densities of the monimolimnion varied due to seasonal temperature changes (Fig. 5). The calculations revealed that in January 2007, the total water density of the monimolimnion was 0.26 g/L higher than in October 2006. However, in January 2007, the density contribution of solutes was about 0.08 g/L lower than in October 2006.

## Conclusions

Using the example of the meromictic Waldsee, we developed a procedure to quantify the density contribution of solutes from chemical analyses. On the basis of molal volumes, the concentration of a solute could be directly linked with its density contribution. Calculations proved that in this iron-meromictic lake, the chemical density gradients were mainly caused by  $\text{Fe}^{2+}$  and the carbonate system ( $\text{HCO}_3^-$  and  $\text{CO}_2$ ). The only gas that was important to density was  $\text{CO}_2$ . Furthermore, DOC and  $\text{Ca}^{2+}$  only contributed a little (7 or 8 %) to the maintenance of the chemical density gradient. Other solutes, such as  $\text{SO}_4^{2-}$ , delivered constant density contributions throughout the whole water column, and were irrelevant to maintenance of the permanent stratification.

In Waldsee, the density gradients caused by solutes between mixolimnion and monimolimnion were low and nearly constant throughout the year. However, they were

sufficiently high to sustain the meromictic state of the lake. Seasonal variations in density differences between mixolimnion and monimolimnion originated primarily from temperature fluctuations. Whereas temperature dominated the density stratification in summer, the stratification in winter was solely sustained by chemical gradients, even against adverse temperature effects.

In Table 1, we present specific density fractions of basically all of the density relevant solutes in fresh water for straight forward use by limnologists at their lakes. Our approach is a tool that can be included in numerical lake models to help to predict the formation, prospective development, and breakdown of meromixis. Such prognoses have important ecological and economic consequences in discussions associated with meromixis, such as the use of monimolimnia for permanent deposition of heavy metals or the effects of climate change on the development of lake stratification.

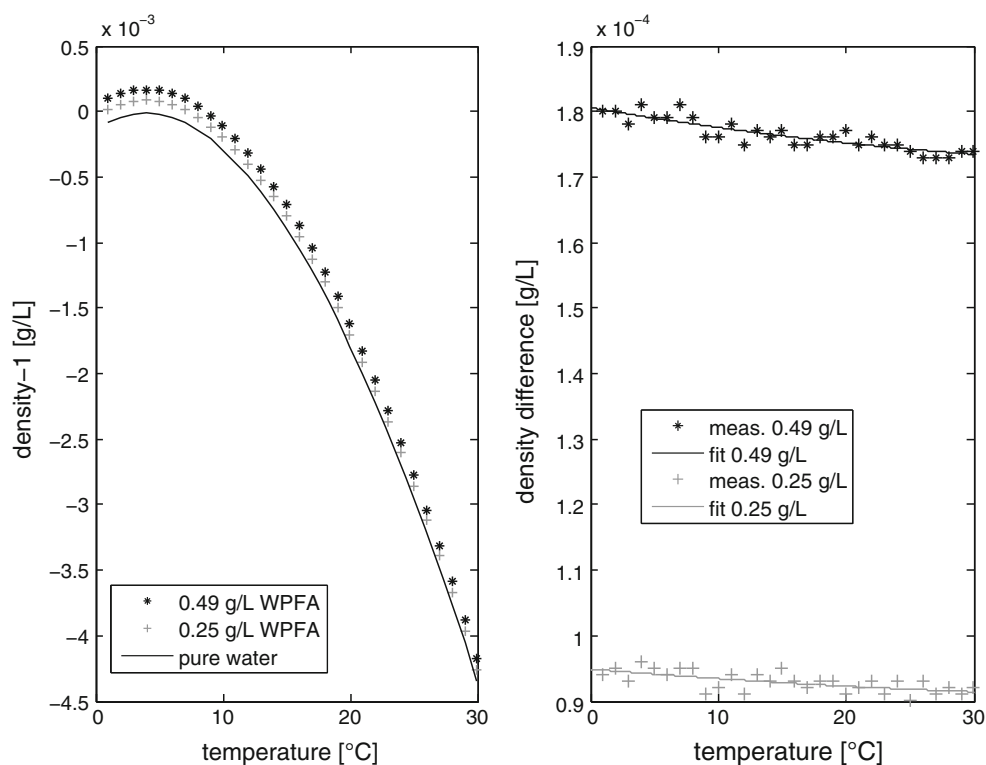
**Acknowledgments** This study was financially supported by Deutsche Forschungsgemeinschaft (DFG).

## Appendix

### Experimental Determination of the Density Contribution of Waskish Peat Fulvic Acid to density

We dissolved 0.00980 g of IHSS Waskish peat fulvic acid (WPFA) in 0.02 L of pure water. According to IHSS

**Fig. 6** Density of IHSS Waskish peat fulvic acid solution against temperature (left panel) and density difference of solutions compared with pure water (symbols) and the second order regression for numerical evaluation (right panel)



**Table 3** Coefficients  $a_i$  for the calculation of the density contribution of dissolved organic carbon (units of the coefficients,  $a_i$ ) were dropped for better legibility

Reference for concentration	Units of $\gamma_{\text{Doc}}$	$a_0$	$a_1$	$a_2$
Mass of dissolved organic matter	$\frac{\text{g/L}}{\text{g/L}} = 1$	0.39	−0.00038	0.000007
Mass of the dissolved organic carbon portion	$\frac{\text{g/L}}{\text{g DOC/L}}$	0.67	−0.00066	0.000012
Molar concentration of dissolved organic carbon	$\frac{\text{g/L}}{\text{mol DOC/L}}$	0.056	−0.000055	0.0000010

(2008), carbon contributes 53.17 % of the mass, yielding a concentration of 0.261 g/L DOC in the solution. The density of the solution was measured using a PAAR DSA 5000 (Austria) densitometer. A  $u$ -shaped glass tube filled with the respective solution is set into vibration and its frequency is measured. The higher the mass inside the tube, the slower is the oscillation. Hence, as the volume is known or calibrated using pure water, the device performs a direct measurement of the density of the contained liquid.

The temperature of the limnologically most interesting temperature interval from 0 to 30 °C was scanned in steps of 1 °C (results see Fig. 6). The same measurement was performed with purified water. The temperatures between both measurements coincided within 0.001 °C. Hence we could calculate the density difference between both measurements, which is attributed to the dissolved Waskish peat fulvic acid (see also Fig. 6). A second order regression was performed to include the (small) temperature signature of the density contribution, which may be neglected for most purposes. The coefficient for various temperatures can be calculated according to:

$$\gamma_{\text{DOC}}(T) = a_0 + a_1(T - 25 \text{ }^{\circ}\text{C}) + a_2(T - 25 \text{ }^{\circ}\text{C})^2$$

The density contribution can be related to various references for concentrations. Concentrations of organic matter are either given in mass of organic matter per volume or mass concentration of DOC, i.e. the concentration of the carbon constituent, or finally as molar concentration of carbon. According to IHSS (2008), carbon contributes 53.17 % of the mass; hence we can supply the coefficients also referring to concentration of carbon (mass or molar concentration) (Table 3).

A second measurement at about half the concentration of IHSS Waskish peat fulvic acid (0.005 g/L, see also Fig. 6) yielded very similar results for the coefficients, only about 3 % higher and a very similar, small temperature effect, which is all clearly within the accuracy at which such solutions can be produced and coefficients be evaluated.

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