Density measurements in mining lakes

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Introduction

Post mining pit lakes vary in their contents of dissolved substances (Schultze & Geller 1996, Schimmele 1995a). Especially the strongly acidified lakes ($pH < 3$) show high concentrations of sulphate and iron (Friese et al. 1998). The chemical composition influences the measurement of some properties, e.g. electrical conductivity (Schimmele 1998), in these waters. Furthermore it affects directly the density structure and the light climate and therefore the stratification, the biological development, and the formation of oxic/anoxic layers (Schimmele 1995b). This paper deals with the influence of dissolved substances on density in mining lakes. Particles and especially the internal production of particles are not considered.

Methods

Water samples were taken at various depths and at various seasons and transported to the laboratory cool and dark. Samples, where reaction with air could change conductivity or density, respectively, were treated under Argon – atmosphere. For density measurements 7 ml of the samples were injected in an temperature - controlled u-tube-oscillator (Anton Paar, Graz, Austria) by a syringe. Oscillation frequencies were determined at least 5 times and averaged. Due to outgassing at higher temperatures and particles in the samples, which disturb the measurement, relative uncertainties were usually about $2\cdot10^{-5}$ - $5\cdot10^{-5}$ (instead of $2\cdot10^{-6}$ for clear water) with higher values at higher temperatures. The uncertainties of el. conductivity $\kappa25$ stem mainly from the temperature correction and are about 1% or less (see Schimmele 1998). The contribution of gases to density in air saturated samples is in the order of $3\cdot10^{-6}$ (Millero & Emmet 1976). Therefore in this case the major effect of outgassing of surface samples is the disturbance of the measurement itself. Chemical analysis are described in Herzsprung et al. (1998) and Friese et al. (1998).

Results and discussion

Figure 1 shows the relation between el. conductivity $\kappa25$ and density at 5°C together with calculations from temperature and el. conductivity after Bührer & Ambühl (1975) for fresh water and Fofonoff & Millard (1983) for seawater. It can be seen that these relations do not hold for mining lakes. In most cases, measured densities are higher than calculated.

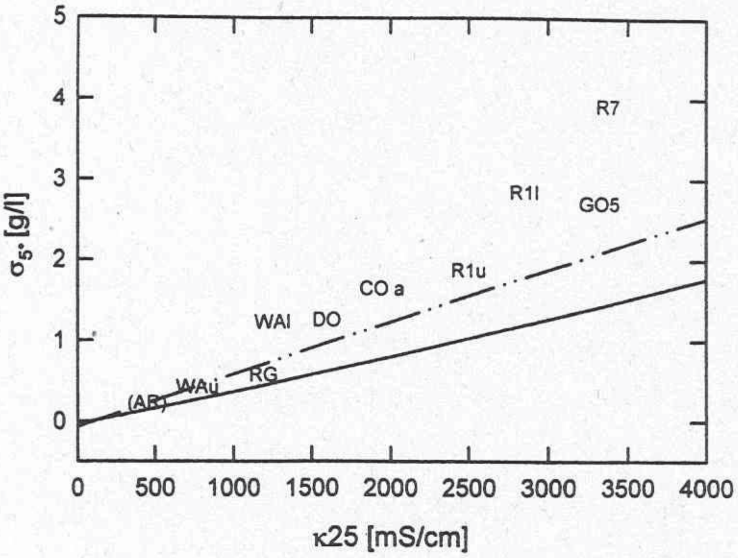

Fig 1: Relation between el. conductivity κ25 and density at 5°C (σ_T = density – 1000 kg·m^{-3}) for samples from various lakes: COa = Cospuden, DO = Döbern, GO5 = Niemegk, R1l = ML111 monimolimnion, R1u = ML111 surface, R7 = ML107, RG = ML117, Wal = Waldsee monimolimnion, Wau = Waldsee surface, (AR) = Arendsee (natural, not a mining lake) and relation according to Bührer & Ambühl (1975; solid line) and Fofonoff & Millard (1983; dash - dotted line). (from Schimmele & Herzsprung 1999)

This may have two reasons. Firstly el. conductivity is not a good estimator for dissolved substances because there is a relative high amount of neutral substances and/or chemical composition changes due to internal processes (see Schimmele & Herzsprung 1999).

Even using the Chen & Millero (1986) formula with input – salinities equal to the sum of measured concentrations of the main constituents yields densities lower than measured (see figure 2; please note, that most of the shown salinities are beyond the upper limit of validity of the Chen & Millero formula of S=0.6).

A look on partial molal volumes helps to estimate the influence of the composition of dissolved substances to density.

The partial molal volume is the change of volume *V* upon the addition of one mole of electrolyte *i* to a large reservoir at constant temperature *T*, pressure *p*, and moles of the other components n_j: $\overline{V}_i^0 = \left(\frac{\partial V}{\partial n_j}\right)_{T,p,n_{j\neq i}}$. In table 1, conventional partial molal volumes $\overline{V}_{conv}^0$ at infinite dilution at 25°C (Millero 1972) are listed, where $\overline{V}_i^0 = \overline{V}_{conv}^0 + z\overline{V}_{H^+}^0$ for cations and $\overline{V}_i^0 = \overline{V}_{conv}^0 - z\overline{V}_{H^+}^0$ for anions. The estimates for the absolute partial volume of the proton $\overline{V}_{H^+}^0$ are varying from -0.9 cm^{3}mol^{-1} to -7.6 cm^{3}mol^{-1} (Millero 1972). Zana & Yeager (1966, 1967, cited by Millero 1972) determined it experimentally to –5.4 ± 2 cm^{3}mol^{-1} at 25°C.

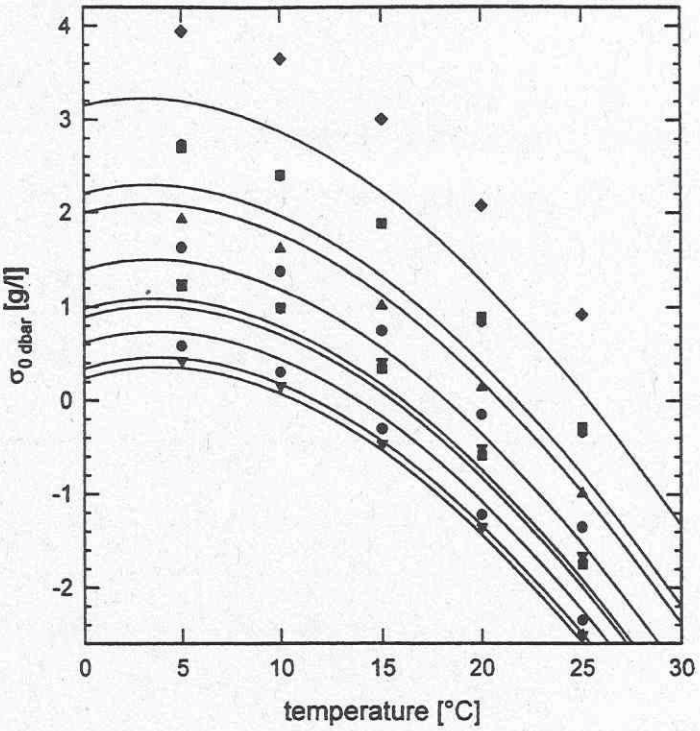

Fig. 2: Measured densities (σ= density – 1000 kg·m^{-3}) for samples from different mining lakes with corresponding calculated densities after Chen & Millero (1972).

Table 1: Conventional partial molal volumes $\overline{V}^0_{conv}$ at infinite dilution at 25°C (Millero 1972)

Ion	$\overline{V}^0_{conv}$ [cm^{3}mol^{-1}]	Ion	$\overline{V}^0_{conv}$ [cm^{3}mol^{-1}]
H^+	0	HCO_3^-	23.4
Na^+	-1.21	Cl^-	17.83
K^+	9.02	CO_3^{2-}	-4.3
Mg^{2+}	-21.17	SO_4^{2-}	13.98
Ca^{2+}	-17.85		
Fe^{2+}	-24.7		
Al^{3+}	-42.2		
Fe^{3+}	-43.7		

For diluted solutions additivity is valid and the relative change in density then is given by $\frac{\Delta\rho}{\rho} = -\sum_j \overline{V}_i^0 m_j + \frac{1}{\rho}\sum_j m_j M_j$, where $m_j = \frac{n_j}{V}$ is the molarity and M_j the molar weight. The first term represents the change of volume and the second represents the increase of density due to the additional mass.

The relative changes in density were calculated for different "typical" mixtures with the values from table 1 and are listed in table 2.

Table 2: Density differences about addition of 1g salt / 1kg water (1 $^0/_{00}$) for different mixtures (under assumption of infinite dilution)

	Ion	Relation	$\frac{\Delta\rho}{\rho} * 10^3$
"seawater"	Na^+	1	**0.72**
	Cl^-	1	
"lake"	Ca^{2+}	1	**0.82**
	HCO_3^-	2	
"mining lake"	SO_4^{2-}	13	**1.05**
	Ca^{2+}	10	
	Fe^{3+}	2	

It can be seen that for the same salinity and different compositions the density change varies widely. The density difference in the above example lies in the same order of magnitude as epi / hypolimnion differences in spring and autumn stratifications of temperate lakes. Furthermore, the molal volumes of the various substances have different temperature dependencies. In figure 3, density measurements from a sample from highly acidic mining lake ML107 (pH ~ 2.3) are drawn at 5 temperatures. In this figure the temperature dependence of pure water (with an additional offset of 4 g/l) and the outcome of the Chen & Millero (1986) formula with a salinity of S=5.0 are added. It can be seen that the true temperature dependence of that specific sample lies in between the both estimates.

Especially in acidic mining lakes, the chemistry is mostly dominated by three species: Ca^{2+}, SO_4^{2-} and Fe^{3+}. Therefore it may be possible to construct equations of state, which hold for groups of mining lakes with only few adjustments.

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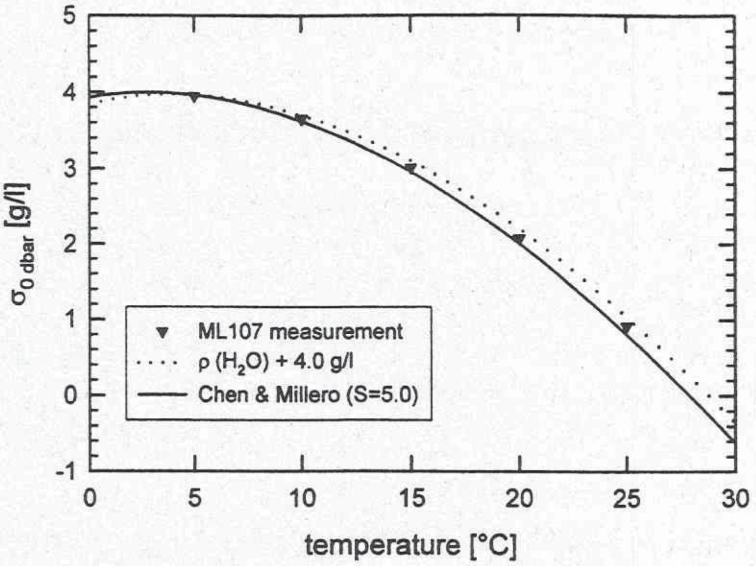

Fig. 3: Measured densities (σ= density – 1000 kg·m^{-3}) for a sample from lake ML107 at various temperatures compared to Chen & Millero (1986) formula with salinity of S=5.0 and pure water with an offset of 4.0 g/l .

References

BÜHRER, H. & AMBÜHL, H., 1975: Die Einleitung von gereinigtem Abwasser in Seen. Schweiz. Z. Hydrol. **37**(2): 347-369.

CHEN ,C.T. & MILLERO, F., 1986: Precise thermodynamic properties for natural waters covering only the limnological range. Limnol. Oceanogr. **31**(3): 657-662

FOFONOFF, N. P. & MILLARD JR., R.C., 1983: Algorithms for computation of fundamental properties of seawater. UNESCO technical papers in marine science **44,** 53pp.

FRIESE, K., HUPFER, M., SCHULTZE, M., 1998: Chemical Characteristics of Water and Sediment. In Acid Mining Lakes of the Lusatian Lignite District. In: Geller, W., Klapper, H., Salomons, W. (Eds.) Acidic mining lakes. Springer Verlag, Berlin, 1998.

HERZSPRUNG, P., FRIESE, K., PACKROFF, G., SCHIMMELE, M., WENDT-POTTHOFF, K., WINKLER, M., 1998: Vertical and Annual Distribution of Ferric and Ferrous Iron in Acidic Mining Lakes. Acta Hydrochim. Hydrobiol. 26 (1998) 5.

MILLERO, F.J., & EMMET, R.T., 1976: The effect of dissolved air and natural isotopic distributions on the density of water. J. mar. Res. 34: 15-24.

MILLERO, 1972: The Partial Molal Volumes of Electrolytes in Aqueous Solutions. In: Horne, R.A. (ed.): Water and Aqueous Solutions, pp 519-564. Wiley, New York.

SCHULTZE, M. & GELLER, W., 1996: The Acid lakes of Lignite Mining District of the former German Democratic Republic. In: R. Reuther (ed.): Geochemical Approaches to Environmental Engineering of Metals. Springer Verlag 1996.

SCHIMMELE, M., 1995a: Zur Schichtungsproblematik in Braunkohlerestseen. DGL Erweiterte Zusammenfassungen der Jahrestagung 1994 in Hamburg: 749-753, Deutsche Gesellschaft für Limnologie, Krefeld, 1995.

SCHIMMELE, M., 1995b: Beeinflussung des Schichtungsaufbaus eines Abgrabungssees durch Wind, Lufttemperatur und Strahlung. In: Geller, W., Packroff, G. (Hrsg.): Abgrabungsseen - Risiken und Chancen. Limnologie aktuell Vol. **7** , S. 91-98. Gustav Fischer Verlag.

SCHIMMELE, M., 1998: Die Messung der elektrischen Leitfähigkeit in Bergbaurestseen. Erweiterte Zusammenfassungen DGL Jahrestagung, Frankfurt a.M., 22. - 26. September 1997: 769-773. Deutsche Gesellschaft für Limnologie, Krefeld 1998.

SCHIMMELE, M. & HERZSPRUNG, P., 1999: Limnology of sulfur acidic lignite mining lakes. I. Physical properties: Influence of dissolved substances on el. conductivity and the density structure. Verh. Int. Verein Limnol. (submitted)

ZANA, R. & Yeager, E. (a) 1966: J. Phys. Chem. **70**, 954; (b) 1967a: J. Phys. Chem. **71**,521; (c) 1967b: J. Phys. Chem. **71**, 4241.

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