

Is Practical Salinity conservative in the Baltic Sea?

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KEYWORDS

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Abstract

The conductivity-salinity conversion algorithm used for oceanographic measurements of Practical Salinity on the PSS-78 scale is designed for IAPSO Standard Seawater. The application of this formula to a given sample of non-standard seawater does not necessarily result in a constant salinity value when the sample's conductivity is measured at different temperatures. We have experimentally studied the magnitude of this non-conservative effect of Practical Salinity using a sample of Baltic seawater possessing a density anomaly of about 50 g m^{-3} . The apparent change of salinity observed is at the limit of experimental uncertainty and is not significantly different from the drift of Standard Seawater, which was measured for comparison.

1. Introduction

The salt dissolved in Baltic Sea water has a well-known chemical composition anomaly, caused mainly by calcium ions discharged from the rivers draining the hinterland (Rohde 1966). Compared to the world ocean, where the density anomaly typically ranges from 20 to 50 g m^{-3} , the Baltic Sea anomaly is relatively large – up to 130 g m^{-3} (Millero & Kremling 1976).

The complete text of the paper is available at <http://www.iopan.gda.pl/oceanologia/>

This anomaly is particularly apparent in the famous Knudsen formula (1901) relating chlorinity Cl to salinity S by the equation:

$$S = 0.03 + 1.805 Cl, \quad (1)$$

which was obtained from a comparison of S and Cl in one sample from the Red Sea, one from the North Atlantic, one from the North Sea and six from the Baltic Sea, including the Kattegat (Millero et al. 2008). For standard seawater from the North Atlantic, the corresponding relation is (Lyman 1969):

$$S = 1.80655 Cl, \quad (2)$$

which is consistent with (1) only for seawater with $S = 35$. Hence, the intercept of (1) resulting from Baltic seawater significantly exceeds the experimental uncertainty of salinity measurements.

The Practical Salinity Scale of 1978 (PSS-78) is derived from chlorinity-conductivity relations measured at diluted or weight-evaporated standard seawater, and converted to salinity by means of eq. (2), as recently discussed in detail by Millero et al. (2008). The conservation of chlorinity, which is evident from the mass conservation of chlorine and bromine when a given sample is heated, pressurised or diluted, is inherited in this way by Practical Salinity as well, if conductivity measurements are performed on standard seawater.

It is unknown how conservative the Practical Salinity definition is in the case when it is measured by a CTD probe in the Baltic Sea under varying in situ conditions if the CTD sensors are routinely calibrated to standard seawater.

If a given sample of standard seawater has a Practical Salinity S_1 at temperature t_1 , then it has – within the experimental uncertainty of PSS-78 – the same salinity $S_2 = S_1$ at any other temperature t_2 . This is true because the empirical formulas for the computation of Practical Salinity were intentionally constructed so as to ensure this conservation (UNESCO 1981). For Baltic seawater, however, the conductivity-temperature relation of a given sample is not the same as for standard seawater. Consequently, a sample of Baltic seawater having an anomalous salt composition with Practical Salinity S_1 at temperature t_1 may show a different Practical Salinity S_2 if measured in the same sample but at another temperature t_2 . The aim of this study was to estimate the potential practical relevance of the difference $S_1 - S_2$.

The term ‘Practical Salinity’ in this paper implies the salinity value returned from standard instruments like salinometers or CTD sensors at any given t and p . In the strict sense of the Practical Salinity definition,

however, any measured sample must be brought to 15°C and 1 atm before its conductivity is measured.

The current paper presents the results of an experimental investigation of this problem. Its conclusion may well be applicable to other coastal or estuarine seas, as well as lakes with similar or smaller composition anomalies.

The SCOR/IAPSO Working Group 127 on Thermodynamics and Equation of State of Seawater is currently preparing a general recommendation of a new salinity scale, the Reference-Composition Salinity Scale 2008, Reference Salinity for short, which constitutes the best available approximation of the absolute salinity of standard seawater (Millero et al. 2008). Consistent with this approach, a new formulation for the thermodynamics of seawater is being developed, expressed in terms of absolute salinity rather than Practical Salinity (Feistel 2007, submitted). For this purpose, the Reference Salinity S_R can in practice be computed from the Practical Salinity S by applying a constant scaling factor:

$$S_R = (35.16504/35) \text{g kg}^{-1} S, \quad (3)$$

which is valid for seawater with the Reference Composition (Millero et al. 2008) and for standard seawater within the experimental uncertainty of c. 0.007 g kg^{-1} .

For regional seawater with salt composition anomalies, the use of the new thermodynamic formulation in terms of absolute salinity will significantly reduce the systematic, anomaly-related errors of computed properties like density as compared to the present use of Practical Salinity as an independent variable. The question arises of how Practical Salinity should be converted to absolute salinity with a minimum error in the case of composition anomalies. Since absolute salinity is conservative by definition, it is necessary to explore whether Practical Salinity measured in a regional seawater is sufficiently conservative to permit a simple linear conversion relation like (3).

For stoichiometric formulations of seawater thermodynamics like the Gibbs-Pitzer function (Feistel & Marion 2007), the natural concentration variable is always the absolute salinity. This semi-theoretical method covers salinities beyond the validity limit $S = 42$ of Practical Salinity and can be applied to arbitrarily composed saline systems in limnology and oceanography.

This paper is organised as follows. In the ‘Material and methods’ section, we describe the experimental set-up and treatment of the seawater sample. In the ‘Results’ section, we present the results of the measurements of Practical Salinity and of density of the same Baltic seawater sample at different temperatures, with IAPSO Standard Seawater as a reference. In

the ‘Discussion’ section, we formulate the conclusion we draw from the experiment.

2. Material and methods

In May 2007, a sample of Baltic seawater was collected from an area of the Pomeranian Bay east of the island of Rügen. A 100-litre barrel was filled with this surface water, hermetically sealed, and transported to the calibration laboratory of the Leibniz Institute for Baltic Sea Research, IOW. This large volume of water was necessary to ensure that the inevitable evaporation effects during the measuring period remained irrelevant.

The Practical Salinities S of the Baltic seawater and of IAPSO Standard Seawater (S near 10) were measured by means of three salinometers (Autosal B Guildline). Two Autosal B devices (Sali2 and Sali3) were operated at 6 different bath temperatures of 18, 21, 24, 27, 30 and 33°C. One salinometer (Sali1) was always kept at a bath temperature of 24°C in order to monitor the stability of the measurements. Additionally, the densities of the samples were measured directly with a vibration densitometer (DMA5000; Anton Paar) at 20°C.

After each setting of the temperature, at least 20 hours were allowed for thermal equilibration.

Most measurements were done in an air-conditioned laboratory at $(23 \pm 0.5)^\circ\text{C}$. Only for the bath temperature of 18°C was the ambient temperature reduced to 18°C. This was necessary because the thermoelectric cooling units of the salinometer were not powerful enough to cool the bath to below the ambient temperature. At larger temperature differences between the sample and the bath, special care had to be taken to appropriately adjust the filling rate into the salinometer. If the filling rate is too fast, too little time may be available for complete heat exchange between the bath and the sample, which may lead to errors in the measurements.

Before the measurements, the temperatures of the salinometer baths were determined by two Standard Platinum Resistance Thermometers (SPRT) connected to a precision resistance meter (MKT 25; Anton Paar). For calculating the Practical Salinity the bath temperatures, measured in terms of the International Temperature Scale of 1990 (ITS-90), had to be converted to the International Practical Temperature Scale of 1968 (IPTS-68); the computation of the Practical Salinity according to the Practical Salinity Scale 78 (PSS-78) requires the temperature values to be given in IPTS-68. In the oceanographic range the transformation can be done with sufficient accuracy with the formula (Saunders 1990, Saunders et al. 1991, Mamayev et al. 1991):

$$t_{68} = 1.00024 t_{90}. \tag{4}$$

Here, t_{68} is the temperature in °C according to IPTS-68, and t_{90} the temperature in °C according to ITS-90.

The successive steps, carried out repeatedly during the measurement procedure, were:

- Setting the salinometer bath temperature;
- Thermal equilibration (at least 20 hours);
- Standardising the salinometers with Standard Seawater (P-series);
- Density measurement of Standard Seawater (P-series);
- Measurement of bath temperatures;
- Salinity measurements of Standard Seawater (10L-series);
- Density measurement of Standard Seawater (10L-series);
- Gently rocking the barrel to eliminate thermal stratification;
- Salinity measurement of Baltic seawater;
- Density measurement of Baltic seawater.

The measurements of Baltic seawater were done using a peristaltic pump. A special screw was mounted in the top cap of the barrel, and a hose was inserted into the centre of this screw and tightened by a rubber seal. The screw was unfastened only during measurements to prevent evaporation. The end of the hose was near the centre of the barrel.

To investigate the potential effect of a vertically inhomogeneous salinity distribution, the barrel was left at rest for 24 hours. Then the opening of the hose was moved carefully to the bottom of the barrel. From this level the water was pumped to the salinometers. The procedure was repeated with the end of the hose located near the top of the barrel. Both values were compared.

3. Results

The density anomaly of the Baltic seawater was determined first. The density measured at 20°C was 1 004 432 g m⁻³. The density calculated from S (Sali1) at 20°C was 1 004 378 g m⁻³. A difference of 54 g m⁻³ was found, which is typical of Baltic surface water but high with respect to open ocean anomalies. The standard uncertainty of c. 10 g m⁻³ of the instrument is significantly smaller.

The mean differences in Practical Salinity S due to the spatially inhomogeneous distribution compared to measurements in the centre of the barrel were -0.0002 (centre-bottom) and 0.0012 (centre-surface). Table 1 shows the result of the vertical gradient measurement in the barrel.

Table 1. Vertical distribution of the Practical Salinity of Baltic seawater in the barrel; S_b : Practical Salinity measured at the bottom without stirring, S_s : Practical Salinity measured 5 cm beneath the surface without stirring, S_c : Practical Salinity measured at the centre with stirring

Device	t [°C]	S_b	S_s	S_c	$S_b - S_s$
Sali1	24	8.1341	8.1330	8.1338	0.0011
Sali2	30	8.1355	8.1340	8.1353	0.0015
Sali3	33	8.1357	8.1341	8.1357	0.0016
$S(33^\circ\text{C}) - S(24^\circ\text{C})$		0.0016	0.0011	0.0019	0.0005

Although the bottom-surface salinity differences in the far right-hand column of Table 1 are at the resolution limit of the instruments, these differences are all similar and systematically positive rather than randomly scattered. This apparently weak stratification is hydrostatically stable, so we conclude that even small salinity differences are reflected by the experimental set-up in a reasonable manner. All salinity differences found between the different temperatures, as shown in the bottom row, are of a similar magnitude and have definite signs. Even if this result is at the limit of instrumental resolution, it hints at a possible non-conservative effect of Practical Salinity of the order of $0.001/(10^\circ\text{C})$. This effect can in principle be resolved over a temperature range of $0\text{--}40^\circ\text{C}$, but this was not possible with the given experimental set-up. But even if this assumed non-conservative effect could be verified in a suitable way, the resulting maximum effect in the Baltic Sea between 0°C and 20°C would not exceed some 0.002 in Practical Salinity, which is irrelevant in practice.

The time-dependent changes (scatter, drift) were found to be about 0.0010 in Practical Salinity (10L Standard Seawater). To show the time-dependent changes in density (10L Standard Seawater), the results of Sali1 (bath temperature always 24°C) and the results of the density measurements for Baltic seawater and IAPSO Standard Seawater are shown in Figures 1–4.

The manufacturer of the salinometer states an accuracy of ± 0.002 in Practical Salinity. The absolute uncertainty for density measurements is quoted as being 10 g m^{-3} . As a result of regular comparison measurements with pure water, the relative uncertainty could be improved to 5 g m^{-3} .

The temperature-dependent changes of S in the $18\text{--}33^\circ\text{C}$ range were found to be 0.0027 (Sali2), 0.0017 (Sali3) for IAPSO Standard Seawater, and 0.0017 (Sali2) and 0.0014 (Sali3) for Baltic seawater. Thus, like IAPSO Standard Seawater, the Practical Salinity of Baltic seawater is conservative to within the uncertainty of the measurements.

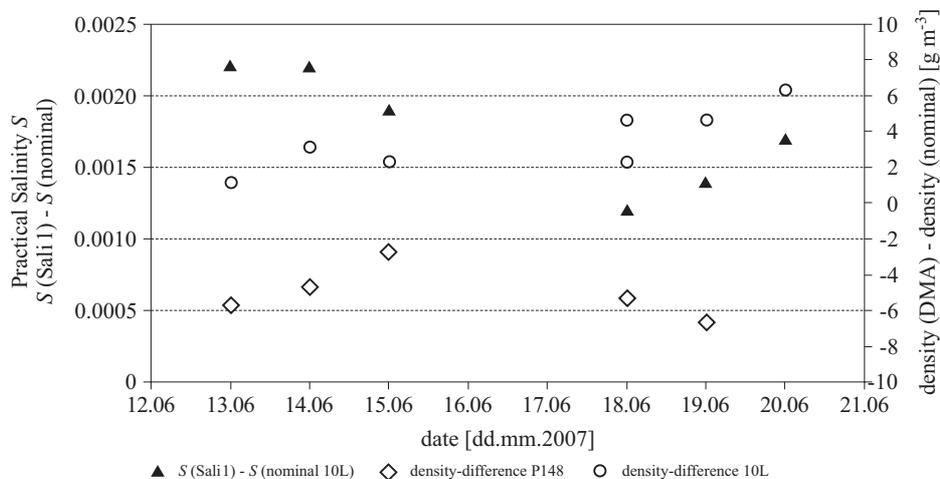


Figure 1. Monitoring the stability of the measurements. The discrepancy is shown between measured Practical Salinity (Salinometer 1 at 24°C) and the quoted salinity of IAPSO Standard Seawater ($S = 10$), as are the density differences determined by a densitometer at $t_{90} = 20^{\circ}\text{C}$ compared to the density calculated from the nominal values of the label. P148: IAPSO Standard Seawater ($S = 35$), 10L: IAPSO Standard Seawater ($S = 10$). The observed discrepancies lie within the experimental uncertainty, confirming that the instrument readings were accurate and stable over the experimental period of time

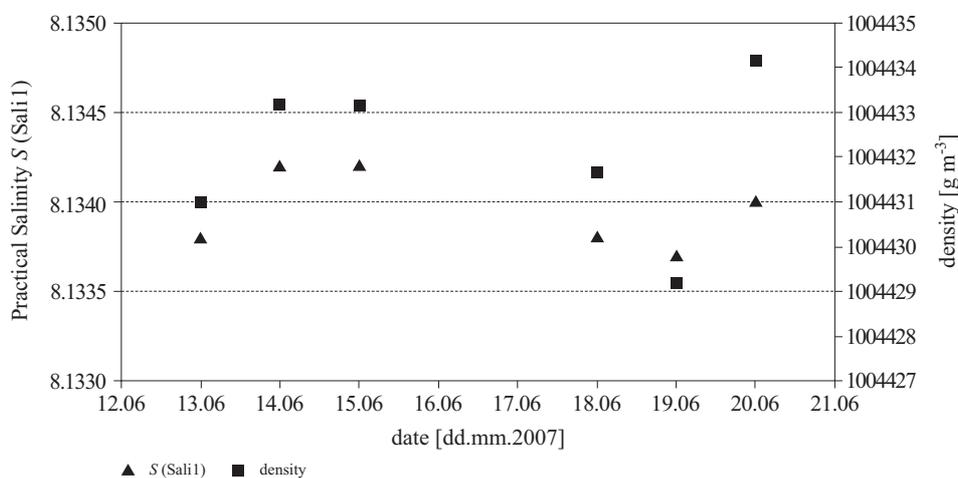


Figure 2. Measurement stability check of Baltic seawater in a 100-litre barrel, measured with Salinometer 1 at $t_{68} = 24^{\circ}\text{C}$ and with a densitometer at $t_{90} = 20^{\circ}\text{C}$. The discrepancies lie within the experimental uncertainty

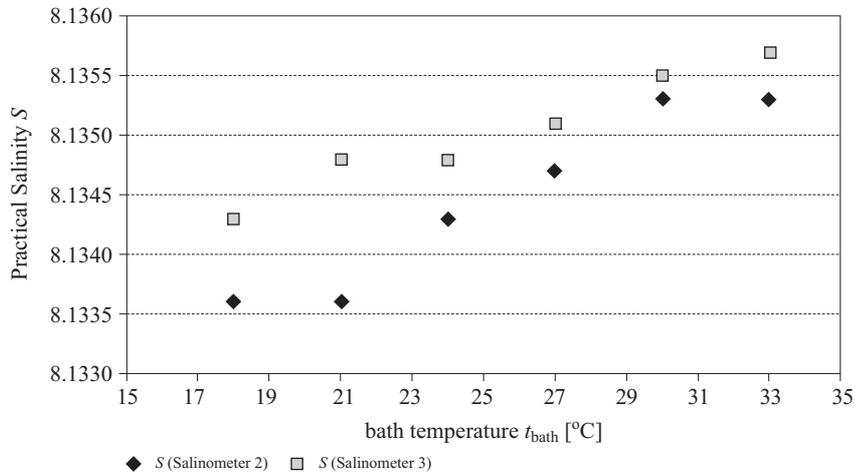


Figure 3. Practical Salinity of Baltic seawater measured with two salinometers at different bath temperatures. The systematic increase of Practical Salinity by 0.0015 over a 15°C temperature difference measured by both salinometers is non-conservative, even though the magnitude of the effect is at the limit of the instrument’s resolution

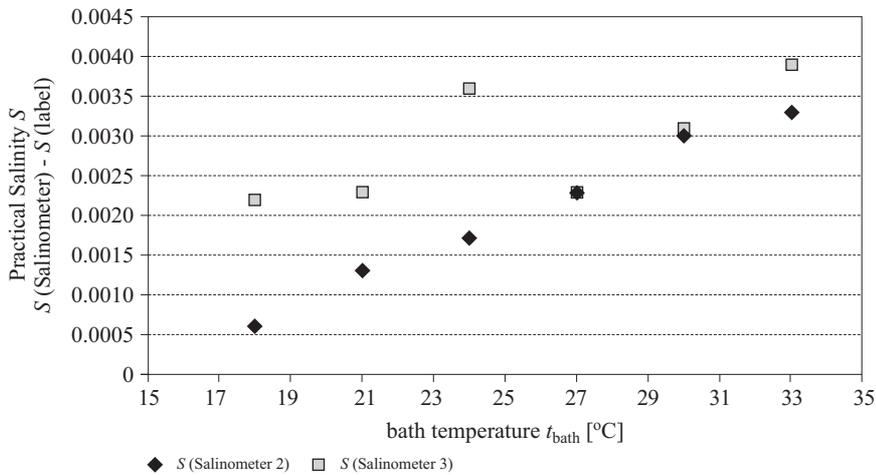


Figure 4. Practical Salinity of IAPSO Standard Seawater ($S = 10$) measured with two salinometers at different temperatures. Here, the differences between the measured values and the values given on the bottle labels are displayed. Though unexpected, the non-conservative increase in Practical Salinity over temperature is at the instrument’s resolution limit and appears to be differently pronounced in the particular samples

4. Discussion

The effect of the temperature-dependent alteration of Practical Salinity S shows no significant differences between Standard Seawater and Baltic seawater. The detected deviations are in the same range as the measurement uncertainty of the salinometer. Assuming that Standard Seawater of the 10L-series is of the same quality as that of the P-series, the uncertainty of the k15-value is 1×10^{-5} (Bacon et al. 2007).

The slight systematic non-conservative drift of Practical Salinity over temperature observed for Baltic seawater as well as for IAPSO Standard Seawater does not exceed the instrument's uncertainty. Thus, in the temperature range studied with Baltic seawater samples having a 50 g m^{-3} density anomaly, no practically relevant non-conservative behaviour could be detected.

By comparing direct densitometer measurements with density, computed from the equation of state taking measured Practical Salinity as the input variable, the Baltic Sea density anomaly can be determined with certainty. A hypothetical alternative detection of this anomaly from the expected non-conservative temperature effect has turned out to be not possible. For this effect, the temperature dependence of conductivity (i.e. the slope of the curve) must differ significantly between standard seawater and seawater with an anomalous chemical composition. No systematic study of this effect has been reported in the literature. We have shown experimentally that the impact of the excess calcium ions known to be present in Baltic seawater (Rohde 1966) do not sufficiently modify the conductivity curve of standard seawater to cause significant non-conservative behaviour.

The newly defined Reference-Composition Salinity Scale (Millero et al. 2008) is rigorously conservative with respect to changes in the sample's temperature, pressure or pure-water content. To use it, the linear conversion formula (3) from Practical Salinity is recommended for IAPSO Standard Seawater. Here we have shown that this formula may also be used for anomalous Baltic seawater without causing significant violations of salinity conservation.

It is recommended that similar studies be carried out in other systems, e.g. limnic ones, in which solute compositions deviate strongly from those of Standard Seawater. The expected non-conservative results obtained from the application of the Practical Salinity Scale 1978 to conductivity measurements of limnic systems should be included in the uncertainty estimate of this method, or else a related temperature correction should be applied to regular measurements at varying water temperatures.

Acknowledgements

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