

Density and Absolute Salinity of the Baltic Sea 2006-2009

R. Feistel, S. Weinreben, H. Wolf, S. Seitz, P. Spitzer, B. Adel, G. Nausch, B. Schneider, D.G. Wright

Final Response (Author Comment)

The authors thank the reviewers for their hints and comments. They will be considered in the revised paper.

Referee #1:

The submitted paper reports the difference between the densities of Baltic Sea samples obtained from direct density measurements on the one hand, and computed from the equation of state on the other hand. The observed difference is attributed to a composition anomaly of the salt dissolved in the Baltic Sea compared to Standard Seawater.

The water of the Baltic Sea is inflow water from the North Sea that possesses negligible composition anomalies, mixed with freshwater. Since the composition anomaly is caused by the freshwater composition, the measured density anomaly can in lowest order be assumed to be proportional to the freshwater fraction of the samples. This assumption was applied in the simple correlation equations derived from the data, similar to the analysis made by Millero and Kremling 30 years ago. Up to this point, the method applied does not rely on any particular property of the freshwater part, neither its origin nor its composition, its variability or its age.

The majority of the freshwater in the Baltic is from river discharge, so we used “river water” synonymously with freshwater. The residence time of 10-30 years implies that the largest fraction of freshwater found in a given sample is not “fresh”, i.e. immediately discharged from a river, rather, it is aged in different water bodies over years or decades. From the data scatter of the correlations it is evident that the properties of the freshwater fraction are not independent of its age, its history or its origin. In this sense, the freshwater aging process includes also sinks or sources or interaction with the sediment or the atmosphere. We did not intend to resolve the complex processes that are responsible in detail for the scatter observed, except for the simple conservative mixing with standard ocean water.

Regarding the sulphur budget in particular, the loss of sulphate by the formation of hydrogen sulphide occurs only temporarily and locally, since it is a reversible process; it does not affect the sulfate/salinity relationship in oxic waters. Of course we have to consider that under anoxic conditions some hydrogen sulphide is bound as iron sulphide. Without having exact data regarding this process, we do believe that it is insignificant in our context.

Referee #2:

It is true that the conditions in the Baltic Sea can serve as a “magnifying glass” for the problems we may encounter in the ocean when more data on composition anomalies will be available that cover the globe more densely and extend over many decades. The effects in the Baltic are measured easier and the relevant time scales are shorter. Given this, the complex processes responsible for composition anomalies and for the spatial and temporal variations of these anomalies are far from being well understood, even in a small estuary such as the Baltic. The effect of composition anomalies on the conductivity, i.e. the Practical Salinity, is considered in quantitative detail in the paper of Rich Pawlowicz, www.ocean-sci-discuss.net/6/2861/2009/. The effect of such anomalies on thermodynamic properties was

studied by Frank Millero in several papers, e.g. by using Young's rule. A new approach to this problem is possible by Pitzer models, see e.g. Feistel & Marion cited in the paper.

1. The true Absolute Salinity is defined in terms of the mass fraction of dissolved material in seawater (Millero et al., 2008). As discussed by Millero et al. the precise definition requires the determination of equilibrium conditions at specified temperature and pressure and even with these additional qualifiers some ambiguity remains. In practice, measuring the mass fraction of dissolved material in seawater is even more difficult than defining it and approximate approaches must be used. It is the "Millero Rule" that says that the density of an aqueous solution is in good approximation a function of the Absolute Salinity, independent of the particular composition of the given mass of dissolved matter (Millero, 1974; Millero et al., 1978, 2008, 2009). Under this approximation, Baltic seawater and Standard Seawater have the same Absolute Salinity if they have the same density (at given T and P). Thus, we measure the density of Baltic seawater, and use the equation of state to compute the Absolute Salinity of Standard Seawater with this density. We then use Millero's Rule and take this "density salinity" as an estimate for the mass of salt dissolved in the Baltic Sea sample. We note however that the true Absolute Salinity is defined as the mass ratio of dissolved material and that Millero's Rule provides an approximation to this quantity. Unfortunately, for seawater that is not of Reference Composition there is currently no method available to precisely measure the Absolute Salinity, but Millero's Rule provides an approximation that allows the density to be recovered to the measurement accuracy (by definition) as well as a useful approximation for other thermodynamic quantities that can be determined from the Gibbs function.
2. The Baltic has a mean basin-scale circulation that is predominantly estuarine (vertical) rather than a horizontal. Precipitation and fresh riverine water is added to the surface, and over time the surface water is enriched with salt from below by entrainment. The permanent upward salt transport through the halocline at about 60 m depth can be estimated as $30 \text{ kg m}^{-2} \text{ yr}^{-1}$ (Feistel et al., 2008; Reissmann et al., 2009). Consequently, the climatological surface salinity increases following the mean surface flow from the north-east to the south-west. Brackish surface water is present in the outflow branch of the Baltic "conveyor belt" that drives the Baltic Current along the Norwegian coast; saltier water from the North Sea is flowing in at the bottom. In the shallow Belt Sea, strong mixing occurs between the inflowing and outflowing layers that implies a recirculation of significant freshwater fractions as a part of the salty bottom water. We shall reconsider the discussion presented in the article.
3. The sample age goes to $d = 1200$ days, Fig. 6.
4. K_{15} is the ratio of the electrical conductivity of the seawater sample, at a temperature (IPTS-68) of 15°C and a pressure of 101325 Pa , to that of a potassium chloride (KCl) solution, in which the mass fraction of KCl is 32.4356 g/kg at the same temperature and pressure. This point will be more clearly stated in the revised article.
5. The variables will be explained as follows:

$$\rho_{\text{pure water measured}} = \rho_{\text{pure water}} (1 + \gamma_{\text{pure water measured}} (\Delta t_{\text{device}} + \Delta t_{\text{reproducibility}}))$$

$$\rho_{\text{seawater measured}} = \rho_{\text{seawater}} (1 + \gamma_{\text{seawater measured}} (\Delta t_{\text{device}} + \Delta t_{\text{reproducibility}})) .$$

$\rho_{\text{pure water measured}}$ and $\rho_{\text{seawater measured}}$ are the densities indicated by the measuring device, whereas $\rho_{\text{pure water}}$ and ρ_{seawater} denote the real densities.

6. Frankly, we have no convincing working hypothesis yet so all we can do is note the discrepancy. The observed magnitude and the direction of the deviations since the 1970s appeared unexpected to us.
7. The numbers in brackets are the standard uncertainties of the corresponding digit(s) in front of the opening bracket.
8. The symbols used together with the units are shown in the inset.
9. There is no significant systematic difference between those fits using the data from filtered or unfiltered samples. In Fig. 8, the intercept is 86.8 mg/kg for all 438 data points; it is 87.0 mg/kg for only the 168 filtered (x) samples, and 86.6 mg/kg for only the 270 unfiltered (u) samples.

Additional References:

Millero, F.J.: Seawater as a multicomponent electrolyte solution. *The Sea*, Vol. 5, E. D. Goldberg, Ed., Wiley-Interscience, 3-80, 1974.

Millero, F.J., Forsht, D., Means, D., Giekes, J., Kenyon, K.: The density of North Pacific Ocean waters. *J. Geophys. Res.* 83, 2359-2364, 1978.

Millero, F.J., Waters, J., Woosley, R., Fen Huang, F., Mareva Chanson, M.: The effect of composition on the density of Indian Ocean waters, *Deep-Sea Res. I* 55, 460–470, 2008.

Millero, F.J., Huang, F., Williams, N., Waters, J., Woosley, R.: The effect of composition on the density of South Pacific Ocean waters, *Mar. Chem.* 114, 56–62, 2009.