The Sound Speed Anomaly of Baltic Seawater

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Abstract

The effect of the anomalous chemical composition of Baltic seawater on the speed of sound relative to seawater with quasi-standard composition was quantified at atmospheric pressure and temperatures of 1 to 46 °C. Three modern oceanographic time-of-flight sensors were applied in a laboratory setup for measuring the speed-of-sound difference $\delta \nu$ in a pure water diluted sample of North Atlantic seawater and a sample of Baltic seawater of the same conductivity, i.e. the same Practical Salinity ($S_p=7.766$). The average $\delta \nu$ amounts to 0.069±0.014 m·s⁻¹, significantly larger than the resolution and reproducibility of the sensors and independent of temperature. This magnitude for the anomaly effect was verified with offshore measurements conducted at different sites in the Baltic Sea using one of the sensors. The results from both measurements show values up to one order of magnitude smaller than existing predictions based on chemical models.

1. Introduction

An important issue regarding the quantification of thermodynamic properties of seawater with high accuracy is the natural variability of the relative composition of dissolved solutes. A certain variability of the thermodynamic properties should be connected with this. Although known for more than a century, these property anomalies came more into focus with the recent formulation of the equation of state of seawater (TEOS-10: IOC et al., 2010). TEOS-10 consistently represents all thermodynamic properties of seawater at the high accuracy level required for modern oceanographic research and state-of-the-art modelling. It also supports the investigation of effects associated with composition anomalies. However, for a number of...
properties including the speed of sound, there is a lack of experimental data with sufficient accuracy for a reliable quantification of the anomaly effects.

TEOS-10 refers to Absolute Salinity $S_A$ as a basic input variable which quantifies the total mass of all dissolved species in a unit mass of seawater. However, $S_A$ is not directly measurable in practice. Salinity as a basic oceanographic measurand besides temperature and pressure is commonly determined from CTD measurements (conductivity, temperature, and pressure) according to the Practical Salinity Scale (PSS-78, Perkin and Lewis, 1980). That means that the Practical Salinity $S_P$ as a measure for salinity exclusively refers to electrically conductive solutes. Hence, for the conversion of $S_P$ to $S_A$ at a high accuracy level, the natural variation of the relative composition of solutes as well as the contribution of non-ionic species have to be considered. For the global ocean, this is implemented in TEOS-10 with an anomaly correction based on a mapped data set (McDougall et al., 2012). The salinity anomaly is described as $\Delta S_A=S_A-S_R$, referring to the conductivity based Reference Salinity $S_R=S_P \cdot (35.16504/35)$ g·kg$^{-1}$ as the best estimate of the Absolute Salinity of seawater with a standard composition. Typically, $\Delta S_A$ in the open ocean is small but significant, reaching $\Delta S_A =0.027$ g·kg$^{-1}$ in the northern North Pacific (IOC et al., 2010). This equals a relative deviation of 0.077 % at Standard Seawater salinity. The main sources are additions of nutrients and carbonates (Millero et al., 2008). However, the effect may be larger in coastal and estuarine waters, mainly because of the increased influence of freshwater input from rivers, causing a significant effect on the related thermodynamic properties. Feistel et al. (2010a) state that currently the accuracy of the empirical formulas for thermodynamic properties of seawater is easily limited by such effects.

The Baltic Sea has brackish water, which is influenced by the Ca$^{2+}$ and carbonate dominated freshwater input from various rivers, and is therefore an especially good example. Extensive field measurements and studies on salinity and density shifts due to composition variability in the Baltic Sea have been conducted (e.g. Millero and Kremling, 1976; Feistel et al., 2010b). Feistel et al. (2010a) presented a comprehensive study on thermophysical property anomalies in Baltic seawater based on chemical models of multi-component aqueous electrolytes. One of the conclusions is that particularly the speed of sound and the density should be sensitive to the presence of anomalous solutes. Sound speed is one of the quantities of fundamental interest due to its thermodynamic relation to other properties, e.g. compressibility and density, and because of its large field of technical applications, e.g. in marine acoustics.
In this study we focus on the speed of sound and show measurement results quantifying the sound speed difference which is associated with the anomalous chemical composition of Baltic seawater. We applied modern acoustic time-of-flight sensors from two different manufacturers under controlled laboratory conditions. The sensors, designed for oceanographic in situ applications, provide sufficient resolution to resolve the speed-of-sound anomaly, independently of their reliability for absolute measurements and of the exact manner of sensor calibration.

We also applied one of the sensors in situ during a field campaign in the south-western Baltic Sea and present results from measurements at different sites and depths. The aim was to test the sensor under field conditions as well as to evaluate its principal ability for use as an acoustic in situ detector for the salinity anomaly. The speed-of-sound measurements were carried out simultaneously with CTD casts. On-board measurements of density and Practical Salinity in water samples taken in parallel were conducted for independent estimates of the salinity anomaly.

2. Measurements

For the speed-of-sound measurements we used oceanographic time-of-flight sensors (AML SV XChange OEM, Valeport miniSVS, and Valeport miniSVS OEM, hereafter referred to as SVX, VP, and VP OEM, respectively). The sensors are designed for in situ measurements in seawater under field conditions. They consist of a single Piezo-electric transducer/receiver and a reflector plate, which is kept at distances of 3.4 cm and 10 cm, respectively, by fixed rods. The time of flight is measured as a time interval of a single acoustic pulse travelling along the transducer-reflector path. Table 1 summarizes basic sensor specifications. The speed of sound is calculated directly from the time of flight, based on a calibration in pure water and applying equations of state (EOS). Modern digital signal processing and timing techniques provide the high resolution of the time-of-flight determination.

Because the focus was on the small differences of sound speed, we did not primarily rely on absolute measurements or uncertainties related to the individual sensors and the

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1 Disclaimer: Any mention of commercial products within this study does not imply recommendation or endorsement by PTB.
manufacturer-given built-in methods for time-of-flight determination. It was rather the high
resolution together with the stability which we used for the detection of the anomaly-related
sound speed differences.

In a separate laboratory study on the capability of these sensors, we investigated their
characteristics and accuracies for measurements in different electrolyte solutions and in
natural seawater in the temperature range of 1-50 °C at atmospheric pressure (von Rohden et
al., 2015). The experimental setup described there was also used for the laboratory
measurements in the current study. In summary, the sensors together with two PTB-calibrated
standard platinum resistance thermometers (SPRT) were placed in a sealed, well stirred, and
thermostated 55 liter bath completely filled with the samples. The temperature was stabilized
within ≈1 mK in the vicinity of the sensors during the periods of sound speed recording. The
conductivity was continuously observed as a purity check or to track the stability of the
sample salinity, and to determine the Practical Salinity. The sensors were operated
simultaneously assuring virtually identical conditions. At each preselected temperature, 20 to
40 single pulses were recorded with each sensor at a rate of 1 Hz, and afterwards averaged.
We carried out a thorough recalibration in pure water, including repeated checks over the
period of investigations in seawater samples. Based on this calibration, the speed of sound in
Atlantic seawater and in Baltic water has been measured.

The measurements of the current study aimed at the determination of the difference of the
speed of sound in Baltic and Atlantic seawater. The Baltic sample was taken in the Arkona
Basin (see Fig. 2). The North Atlantic reference sample (NA II) was taken from the surface
close to the permanent station “Kiel 267” (33°N, 22°W) in the Madeira Basin in May 2016.
The location was chosen because of the low nutrient content, as the samples were mainly
intended for laboratory calibration of conductivity probes. We therefore considered the
sample as a substitute for Standard Seawater having reference composition. Before
measurements, the NA II sample was diluted with pure water to virtually the same Practical
Salinity $S_p$ as the original Baltic sample. Besides the adjustment of $S_p$, the same bath
temperatures for the separate measurements were preselected to achieve conditions as similar
as possible for the comparison of the sound speed results.
2.1 Salinity anomaly

Because the sound speed anomaly $\delta c$ is related to the salinity anomaly, we first estimated the Absolute Salinities $S_A$ and the connected salinity anomaly $\delta S$ for our samples. For the diluted North Atlantic water we calculated the Absolute Salinity according to TEOS-10 as $S_{A,\text{cond}}=S_R=S_P \cdot u_{PS}$, based on the conductivity and temperature readings. That is, we assumed standard composition in the diluted sample. We regard this assumption as justified because the salinity anomaly mapped for the North Atlantic region (IOC et al. 2010) can be neglected within the range of our experimental salinity uncertainty.

For the Baltic sample, we first estimated the salinity the same way as for the Atlantic sample, i.e. assuming standard composition. Secondly, we calculated $S_{A,\text{dens}}$ from an independent density measurement. The density was measured repeatedly at 20 °C with an oscillating U-tube densimeter (Anton Paar DSA 5000 M) to $1004.154 \pm 0.004 \text{ kg} \cdot \text{m}^{-3}$. With it the Absolute Salinity $S_{A,\text{dens}}$ was calculated using the TEOS-10 expression $S_{A,\text{dens}}(T, p, \rho)$. Although the expression presumes standard salt composition again, the estimation of the Absolute Salinity from the measured density is assumed to be appropriate for the Baltic sample. This is because the density-salinity relation is virtually insensitive to the exact salt composition as long as the deviations from the standard composition are small. That is, for many common ions, the change in density caused by very small additions is within measurement uncertainty of a similar change in the mass of sea salt. This is the empirical assumption known as Millero’s rule (Millero 2008, Feistel et al. 2010a, b). We identified the difference $\delta S_{A,m}=S_{A,\text{dens}}-S_{A,\text{cond}}$ as the measure for the salinity anomaly of the Baltic sample in g·kg$^{-1}$. Non-conductive solutes which are not included should play a minor role in the case of Baltic water. Our measure for the salinity difference $\delta S_{A,m}$ is easy to access by the above-mentioned routine density and conductivity measurement techniques. Because we can identify $S_{A,\text{dens}}$ as the Absolute Salinity described in TEOS-10, and $S_{A,\text{cond}}$ as the Reference Salinity $S_R$, we can compare $\delta S_{A,m}$ with the parameterization for Baltic seawater given by Feistel et al. (2010a). It is based on conductivity and density measurements in 436 samples taken in 2006–2009, and provides the basis for the calculation of the Absolute Salinity from knowledge of Practical (or Reference Salinity) as single parameter:

$$S_A = S_R + 86.9 \text{ mg} \cdot \text{kg}^{-1} \cdot (1-S_R/S_{SO}),$$

(1)

with the Standard Ocean Salinity $S_{SO}=35\cdot u_{PS}=35.16504 \text{ g} \cdot \text{kg}^{-1}$, and $S_R>2 \text{ g} \cdot \text{kg}^{-1}$. 
The density of the original (not diluted) Atlantic sample was measured to $(1025.688\pm0.004)$ kg·m$^{-3}$. The values of $S_A$ estimated from measured $S_P$ and calculated with TEOS-10 from the density were consistent within the uncertainties, supporting the general validity of the procedures. The density of the diluted Atlantic sample could not be determined because the densimeter was not available at that time. Because standard composition can be assumed for the original and diluted North Atlantic samples, $S_A$ is equivalent to $S_R$ for both, and $S_A$ of the diluted sample is given by the dilution ratio. The results for the relevant salinity and salinity differences are summarized in Table 2. It was confirmed that the density-based salinity anomaly of $0.067$ g·kg$^{-1}$ agrees well with the anomaly of $0.068$ g·kg$^{-1}$ calculated from Eq. (1) within the uncertainty of $0.009$ g·kg$^{-1}$.

### 2.2 Laboratory results for the speed-of-sound anomaly

The dilution of the Atlantic sample resulted in the same Practical Salinity $S_P$ as beforehand recorded in the Baltic sample. Pure water was gently added to the pre-diluted, continuously mixed, and temperature stabilized sample within the thermostat bath while tracking the conductivity. This resulted in a final $S_P$-value practically identical to the Baltic sample (see Table 2). The procedure naturally implies different final Absolute Salinities for the two samples, associated with the sound speed differences of interest.

The sound speed anomaly is given by the direct difference of the measured values, provided that $S_P$, temperature, and pressure are the same at each reading point. Within our uncertainties, this condition was met for $S_P$, which was shown to be virtually identical, and for (atmospheric) pressure. Differences in the preset bath temperatures, however, were relevant. They were included by converting the measured sound speed in the Baltic sample to the bath temperatures of the Atlantic sample before calculating the sound speed difference. The respective local temperature sensitivity $\partial w / \partial T$ was approximated using the average temperature of both samples at each point. Because the differences of the preset temperatures are still small, uncertainty contributions from this approximation, and also from the actual choice of the equation of state applied for the estimate of the local temperature sensitivity $\partial w / \partial T$, were negligible.

The results for the three sensors are shown in Fig. 1 as symbols and listed in Table S1 (supplementary material). Within the scatter, the results from the individual sensors as a whole are indistinguishable, and no significant trend with temperature can be assessed. The
average over the data points from all sensors is \( \delta v = 0.069 \, \text{m} \cdot \text{s}^{-1} \) with a standard deviation of 0.014 m·s\(^{-1}\). Remember that this purely experimental estimate of \( \delta v \) is based on the criterion of equal conductivity in both samples. It is different from using other reference parameters such as chlorinity, density, or Absolute Salinity, which are more difficult to implement in practice. However, a density-related measure for \( \delta v \) can be calculated and compared to the results from the acoustic sensors: Subtraction of TEOS-10 sound speeds using the estimates for the Absolute Salinity in the Baltic (\( S_{A,\text{dens}} \)) and diluted Atlantic (\( S_{A,\text{cond}} \)) sample (Table 2) as arguments yields the line in Fig. 1. This relies on the validity of Millero’s rule with respect to the density-salinity relation. Alternatively, the Absolute Salinity in the Baltic sample can be calculated with Eq. (1) from measured \( S_P \), resulting in 7.871 g·kg\(^{-1}\). This value confirms our density based estimate of \( S_{A,\text{dens}} \) and would accordingly produce a virtually identical curve for \( \delta v \).

### 2.3 Field measurements

We applied one of the sensors (VP) used for the laboratory measurements at three different sites in the south-western Baltic Sea (Fig. 2). Besides basic testing under field conditions, we focused on its general ability to reproduce the small anomaly related \( w \)-effects. The VP sensor was fixed in horizontal orientation close (≈10 cm) to the sensor head of a Seabird SBE 911plus probe equipped with two temperature and two conductivity sensors (calibrated at IOW to 1.5 mK and 0.003 mS·cm\(^{-1}\) \( k=1 \)), respectively), all mounted in an oceanographic sampling rosette.

With this configuration we saved speed-of-sound and CTD data simultaneously in continuous recordings at selected constant depths for typically 2 min at 1 Hz. The sampling depths were chosen by means of previously taken vertical CTD profiles. In parallel to each continuous measurement we filled two 5 liter Niskin water samplers. The samples were measured on-board for density using an Anton Paar DMA 5000 M vibrating tube densimeter relative to pure water (uncertainty 2.5·10\(^{-6}\) g·cm\(^{-3}\), \( k=1 \)), and for Practical Salinity with a Guildline Autosal 8400B salinometer (24 h accuracy ±0.002 PSU \( k=1 \)), adjusted daily with OSIL P155 Standard Seawater). The data are summarized in Table 3 as averages over manually chosen subintervals from the 2-min recordings including standard deviations (CTD), and as averages of the two measured Niskin samples taken in parallel to the CTD measurements (density and \( S_P \)), respectively.
Deviations of $S_P$ from CTD data and salinometer outputs were generally smaller than 0.003 in homogeneous water layers. This gives an upper estimate of the measurement uncertainty for $S_P$. Standard deviations for $S_P$ from CTD measurements were typically one order of magnitude smaller.

Occasionally, much larger variations of CTD and speed-of-sound outputs (with time) at the constant nominal depths were detected. They reflect coactions of local temperature or salinity gradients and surface wave induced movement of the vessel and rosette. The occurrence of complex thermohaline stratification with partially strong vertical temperature and salinity gradients is typical for the deep water in the Baltic. In such cases, the respective data sets have been excluded from further evaluation. Generally we can state that in stratified regions the uncertainty of all measured properties including speed of sound was in most cases dominated by the variability of the in situ conditions in the vicinity of the sensors. However, the existence of the stratified regime in principle provided an opportunity to investigate samples with different salinity and the respective changes of the anomaly effects at one site.

In the same way as described above for the laboratory investigations, we determined the salinity anomaly $\delta S_A$ from the on-board measurements of density and $S_P$ (Table 3, right column). Together with the laboratory estimate and the empirical parameterization (Eq. (1)), $\delta S_A$ is shown in Fig. 3. Based on this consistent picture of the salinity anomaly we evaluated the results from the sound speed sensor in view of the anomalous deviations.

In von Rohden et al. (2015) we documented the existence of certain inconsistencies for speed of sound among the pure water calibrated time-of-flight sensors including the unit used here. These variations were an order of magnitude larger than the reproducibility and showed apparent trends with temperature and salinity. That means that an adequate calibration covering the large Baltic salinity range would be necessary for the comparison of direct sound speed readings. Such a calibration, however, was not appropriate. Hence, a direct detection of $\delta w$ by a simple comparison of the in-situ values with sound speed derived from parallel CTD data using equations of state (assuming standard composition) was not applicable.

Instead, we related the differences of the actual sensor displays to the corresponding EOS-calculated values $(w-w_{\text{EOS}})_{\text{Baltic}}$ with the analogous differences $(w-w_{\text{EOS}})_{\text{Atlantic}}$ which were calculated on the basis of laboratory records in two samples of diluted North Atlantic seawater (as a “substitute” for Standard Seawater):
\[ \delta v = (w-w_{EOS})_{\text{Baltic,in situ}} - (w-w_{EOS})_{\text{Atlantic,Lab}} \] (2)

The first of the reference samples is the one used for the laboratory estimate of \( \delta v \) with \( S_P = (7.765 \pm 0.007) \) (NA II). The second is another Atlantic sample (NA I) diluted to \( S_P = (16.66 \pm 0.03) \), taken from the same location in the Madeira Basin in June 2012. Using these samples we classified the Baltic in situ measurements into two groups by means of salinity in the sense that the two Atlantic reference samples can be seen as representative of the two \( S_P \) ranges (7.3 to 8.4, and 13.3 to 18.8) sampled during our Baltic Sea field trip. Table 3 and Table 4 are accordingly separated into upper and lower parts. The sound speed differences \( (w-w_{EOS})_{\text{Baltic}} \) and \( (w-w_{EOS})_{\text{Atlantic}} \) are listed in Table 4 for both TEOS-10 and the Chen and Millero (1977) equation.

In principle, this proceeding is similar to a “local” recalibration of the sensor in seawater at the two salinities. The approach of relating the Baltic field measurements with the fixed Atlantic reference samples however implies that \( (w-w_{EOS}) \) is basically independent of salinity, at least within both defined salinity ranges. A possible dependence of the difference on pressure should be negligible due to the comparatively weak sensitivity of sound speed to pressure and the rather shallow sampling depths (<43 m). The comparatively strong temperature dependence of the reference differences \( (w-w_{EOS}) \) was considered by interpolation to the Baltic sample temperatures (CTD) using polynomials. An example for the sample with \( S_P = 7.765 \) is given in Fig. 4. The data are also listed in Table S2 of the supplementary material. The results for the extracted sound speed anomaly \( \delta v \) are listed in Table 4 and plotted in Fig. 5. The courses of the differences \( w-w_{EOS} \) reflect the inaccuracy of both the sensor with respect to absolute values, and the actual reference equation. However, due to the high sensor stability and resolution, the uncertainty of \( \delta v \) is expected to be much smaller than the uncertainties of each of the two terms.

As a basic outcome we state that at least over the period of the field campaign (~1 week) the sensor was stable. The data show a smooth course without strong salinity dependence (Fig. 5). Especially the \( \delta v \) at \( S_P = 8 \) reproduce well and independently of the sample site, date, and depth (the cluster of points includes one sample from the site OB at \( \approx 12.5 \) m).

Whereas the outputs of the equations apparently differ by \( \approx 0.05 \) m·s\(^{-1} \) (upper panel of Fig. 5), the estimated sound speed anomaly \( \delta v \) is basically independent of the equation used as a reference (lower panel), which was expected within the assumptions and uncertainties of our
approach. Note that the use of the Del Grosso and Mader (1974) equation as a reference would not be reasonable because of its validity limited to oceanic salinities which do not include the brackish Baltic waters. Although a bit lower, the $\delta w$ at $S_P \approx 8$ match the more accurate laboratory findings within the range of uncertainties (Fig. 1) (discussion below). The high reproducibility of the measurements at $S_P \approx 8$ also implies the validity of the results at higher $S_P$ (13.3 to 18.8), for which no comparative experimental values are available, even though there are somewhat larger uncertainties due to the larger salinity error of our $S_P = 16.66$ reference sample (NA I).

Contributions to the uncertainty of $\delta w$ comprise the general stability of the sensor ($0.019$ m·s$^{-1}$), represented by the reproducibility of calibration measurements in pure water, and the effect of conductivity (salinity), temperature, and pressure uncertainties on EOS calculated sound speed ($<0.04$ m·s$^{-1}$). We assigned an additional contribution of $0.02$ m·s$^{-1}$ to the difference ($w - w_{EOS}$)$_{Atlantic}$ (sensor display minus EOS calculated sound speed), which accounts for the interpolation to the in situ measured temperatures (Fig. 4), and for the assumption of an insignificant salinity and pressure sensitivity of this difference. The limited validity of a vanishing salinity sensitivity might be indicated by the somewhat suspicious $\delta w$ at the $S_P \approx 13.3$ and $S_P \approx 18.8$ with the largest deviations to the reference salinity of $S_P = 16.66$.

The resulting overall uncertainty of the sound speed anomaly $u(\delta w)$ is given in Table 4.

3. Discussion

The results of the laboratory investigations represent the first experimental estimate of the speed-of-sound anomaly caused by the anomalous salt composition in Baltic seawater. Although conducted for only one sample with a Practical Salinity of $S_P = 7.766$, the validity of the extracted $\delta w$ was supported by the consistency of the data measured with three time-of-flight sensors from two manufacturers simultaneously, also at temperatures exceeding the natural range. The results show that with the high resolution and reproducibility of modern time-of-flight sensors, the anomaly effect can be resolved with comparison measurements.

Feistel et al. (2010a) derived a Gibbs function for Baltic Seawater from Pitzer equations using a numerical model (FREZCHEM) which simulates chemical and physical properties of seawater with variable solute composition. With this, the speed-of-sound deviation in Baltic water and seawater with the same electrical conductivity was predicted under the presumption
that the salt anomaly can be represented by additional calcium carbonate coming from river water discharge. The results are shown in Fig. 25 in Feistel et al. (2010a). We reproduced the figure and added our measurement results to the model curves in Fig. 6. Obviously, within the uncertainty our results as a whole do not conform to these predictions. The measurements are better represented by \( \delta w = w_{\text{TEOS}}(S_A) - w_{\text{TEOS}}(S_R) \) (dotted lines in Fig. (6)), where \( S_A \) and \( S_R \) are related to each other according to Eq. (2). That is, they rather follow Millero’s rule (see also Fig. 13 in Feistel et al. (2010a)), and therefore confirm that the sound speed in Baltic Seawater can reasonably be predicted using the Absolute Salinity \( S_A \) with TEOS-10.

From the field measurements in the Baltic Sea and from our separate study (von Rohden et al., 2015) we conclude that modern time-of-flight sensors are not (yet) applicable as a tool for the in situ detection of the salinity anomaly when calibrated in pure water only. To solve this, an extensive calibration in Standard Seawater covering the temperature and the large salinity range of the Baltic Sea or significant improvements of the absolute sensor uncertainty are required.

With the in situ sensor application we showed that in the face of the above restrictions it is possible to give a reliable estimate of \( \delta w \) in a non-routine demonstration. In this way we yielded adequate results for the salinity range of \( S_p \approx 7 \) to 19 and reproduced well the laboratory results at \( S_p \approx 7.766 \) within the uncertainties.

Comparative measurements as shown for the sample in this study may be the way to extend the data set to cover the whole salinity range of the Baltic Sea. However, it must be considered that the salt composition of the freshwater input from the rivershed is geographically, as well as temporally, and with respect to the solute composition, not homogeneous. That means that the anomalous salt component might be variable with respective effects on the magnitude of sound speed deviations, dependent on the time scales of the horizontal and the rather strongly salinity controlled diapycnal exchange processes. This might also be significant for the results of our in situ measurements.

**Data availability**

All relevant data are provided with Tables 2-4 in the manuscript and with two tables in the Supplement.
**Author contributions**

C.v.R designed and carried out the laboratory experiments, supervised the offshore speed-of-sound measurements, evaluated the data, and wrote the manuscript. S.W. prepared the field activities and carried out the on-board density and CTD measurements. F.F. contributed to the data evaluation and manuscript preparation.

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References


Table 1. Sensor specifications. The response times basically reflect the time of flight of sound pulses. The reproducibility corresponds to the standard uncertainty for measurements in pure water in our experimental setup over a period of one (AML) and two years (VP), respectively (von Rohden et al., 2015).

<table>
<thead>
<tr>
<th></th>
<th>AML SVX</th>
<th>VP, VP OEM</th>
</tr>
</thead>
<tbody>
<tr>
<td>acoustic pathlength / mm</td>
<td>68</td>
<td>200</td>
</tr>
<tr>
<td>response time / µs</td>
<td>~47</td>
<td>~140</td>
</tr>
<tr>
<td>time resolution / ns</td>
<td>~0.02</td>
<td>0.01</td>
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<tr>
<td>practical resolution w / m·s⁻¹</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td>reproducibility / m·s⁻¹</td>
<td>0.032</td>
<td>0.019</td>
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</table>
Table 2. Salinity estimates for the samples used, and salinity differences related to the composition anomaly for the Baltic seawater sample, including standard uncertainties.

<table>
<thead>
<tr>
<th>Salinity / g·kg⁻¹</th>
<th>Baltic diluted</th>
<th>Baltic original</th>
<th>North Atlantic diluted</th>
<th>North Atlantic original</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sp / PSU</td>
<td>7.766±0.007</td>
<td>7.765±0.007</td>
<td>36.208±0.01</td>
<td></td>
</tr>
<tr>
<td>Sₐ,cond (assum. standard comp.)</td>
<td>7.803±0.007</td>
<td>7.801±0.007</td>
<td>36.379±0.01</td>
<td></td>
</tr>
<tr>
<td>Sₐ,dens (from measured density)</td>
<td>7.870±0.006</td>
<td></td>
<td>36.381±0.006</td>
<td></td>
</tr>
<tr>
<td>Meas. diff. δSₐ,m=Sₐ,dens−Sₐ,cond</td>
<td>0.067±0.009</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calc. diff. δSₐ,c (Eq. (1))</td>
<td>0.068</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 3. CTD data (averages of 2-min recordings at constant depths) at three sites in the Baltic Sea (see Fig. 2) in August 2014 including standard deviations; \( p \) = hydrostatic plus air pressure. Three right columns: On-board density and salinity measurements as averages of two samples taken in parallel to the CTD measurements; calculated salinity anomaly \( \delta S_A \) based on on-board measurements.

<table>
<thead>
<tr>
<th>Site</th>
<th>Measurements</th>
<th>calc. ( S )-anomaly</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>in situ CTD</td>
<td>On-board</td>
</tr>
</tbody>
</table>
|      | in sit 
|      | \( T \) \( \sigma(T) \) | \( S_p \) \( \sigma(S_p) \) | \( p \) \( \sigma(p) \) | \( \rho \) | \( S_p \) | \( \delta S_A \) |
| °C   | °C           | (PSU)                | (PSU)                  | Pa          | Pa          | g·cm\(^{-3}\) (PSU) | g·kg\(^{-1}\) |
| DS   | 20.855       | 0.001                | 7.899                  | 0.0009      | 166308      | 995                 | 1.004257 | 7.902 | 0.068 |
| DS   | 21.280       | 0.003                | 7.950                  | 0.0001      | 166069      | 777                 | 1.004295 | 7.951 | 0.068 |
| DS   | 20.457       | 0.002                | 8.399                  | 0.0002      | 144747      | 246                 | 1.004633 | 8.401 | 0.065 |
| AB   | 20.995       | 0.001                | 7.773                  | 0.0002      | 133966      | 974                 | 1.004162 | 7.775 | 0.069 |
| AB   | 21.170       | 0.002                | 7.779                  | 0.0002      | 173492      | 185                 | 1.004168 | 7.781 | 0.071 |
| AB   | 21.207       | 0.003                | 7.780                  | 0.0002      | 172901      | 107                 | 1.004169 | 7.782 | 0.071 |
| OB   | 22.105       | 0.002                | 7.320                  | 0.0002      | 134186      | 813                 | 1.003829 | 7.322 | 0.082 |
| OB   | 22.007       | 0.001                | 7.344                  | 0.0003      | 134190      | 603                 | 1.003846 | 7.345 | 0.082 |
| OB   | 21.947       | 0.008                | 7.377                  | 0.0033      | 163016      | 354                 | 1.003867 | 7.373 | 0.080 |
| OB   | 20.701       | 0.005                | 7.518                  | 0.0003      | 225661      | 205                 | 1.003973 | 7.513 | 0.080 |
| OB   | 20.786       | 0.017                | 7.524                  | 0.0003      | 225723      | 190                 | 1.003979 | 7.525 | 0.077 |
| DS   | 15.192       | 0.001                | 17.849                | 0.0024      | 291574      | 535                 | 1.011767 | 17.846 | 0.046 |
| DS   | 14.999       | 0.004                | 18.176                | 0.0044      | 275119      | 405                 | 1.011944 | 18.078 | 0.049 |
| DS   | 14.685       | 0.002                | 18.775                | 0.0007      | 293951      | 103                 | 1.012462 | 18.764 | 0.046 |
| AB   | 15.925       | 0.005                | 13.833                | 0.0096      | 503236      | 153                 | 1.008710 | 13.796 | 0.058 |
| AB   | 15.081       | 0.002                | 13.293                | 0.0040      | 479620      | 69                  | 1.008288 | 13.241 | 0.056 |
| AB   | 15.801       | 0.004                | 14.265                | 0.0039      | 505692      | 87                  | 1.009059 | 14.262 | 0.055 |
| AB   | 15.709       | 0.006                | 14.276                | 0.0029      | 508273      | 84                  | 1.009070 | 14.274 | 0.057 |
| AB   | 14.230       | 0.001                | 16.723                | 0.0002      | 531733      | 405                 | 1.010919 | 16.721 | 0.052 |
Table 4. Speed of sound measured with the time-of-flight sensor in the Baltic Sea (in m·s⁻¹);

`w`-differences (measured minus calculated) using TEOS-10 and Chen and Millero (1977) for
the Baltic in-situ measurements, and for the laboratory measurements in samples of natural
Atlantic seawater with $S_P$=7.765 (upper part of table) and $S_P$=16.66 (lower part). The
differences in the Atlantic samples were previously interpolated to the Baltic in situ
temperatures. $\delta w$ are the respective estimates of the sound speed anomaly according to Eq.
(2). The uncertainty estimate $u(\delta w)$ (right column) is virtually the same for both reference
equations. The data are in the same order as in Table 3.

<table>
<thead>
<tr>
<th>Site</th>
<th>measured sound speed</th>
<th>rel. to TEOS-10</th>
<th>rel. to Chen and Millero (1977)</th>
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<tr>
<td></td>
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<td>Baltic</td>
<td>Atlantic</td>
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<tr>
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<td>w</td>
<td>$\sigma(w)$</td>
<td>$w-w_{TEOS}$</td>
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Figure 1. Speed-of-sound differences associated with the salinity anomaly for Baltic seawater at $S_p=7.766$. Symbols: Measured differences from the Baltic and the diluted Atlantic sample (NA II) with virtually the same $S_p$. Uncertainty bars are exemplary given at 4 °C. Line: $\delta v$ calculated as $\delta v = v_{\text{TEOS10}}(S_{A,\text{dens}}, T, p_0) - v_{\text{TEOS10}}(S_{A,\text{cond}}, T, p_0)$. The shaded area denotes the uncertainty range due to the salinity uncertainty.
Figure 2. Measurement and sampling sites in the south-western Baltic Sea. DS = Darß Sill, AB = Arkona Basin, OB = Oder Bay.
Figure 3. Salinity anomaly, determined from density and salinity measurements, vs. Reference Salinity $S_R = S_P + u_{PS}$. Filled symbol: laboratory sample; Open symbols: Baltic field samples. The straight line shows the parameterization of Feistel et al. (2010b), Eq. (1), for comparison.
Figure 4. Time-of-flight sensor output relative to speed of sound calculated with TEOS-10 and Chen and Millero (1977) equations of state, exemplary for the North Atlantic seawater sample with $S_T=7.765$ (laboratory measurements). The lines show polynomial fits used for interpolation to extract values according to the in-situ temperatures of the Baltic field measurements.
Figure 5. Upper panel: Measured speed of sound (Baltic) relative to calculated values with equations of TEOS-10 and Chen and Millero (1977) for the same ($S_p$, $T$, $p$). The displacement between both reflects differences in the outputs of the equations. Lower panel: Speed-of-sound anomaly $\delta w = (w_{\text{EOS}})_{\text{Baltic, in situ}} - (w_{\text{EOS}})_{\text{Atlantic, ref}}$ (upper panel “minus” Fig. 4).
Figure 6. Experimental data for sound speed anomaly $\delta \nu$ in Baltic seawater (symbols) in comparison to model results (curved lines, reproduced from Fig. 25 in Feistel et al., 2010a) at atmospheric pressure. Filled symbol: average of laboratory measurements in a sample with $S_R=7.803 \text{ g kg}^{-1}$ ($S_P=7.766$) at temperatures of 1 to 46 °C. Open symbols: data derived from off-shore measurements, see Fig. 5. The dotted lines show $\delta \nu = \nu_{\text{TEOS10}}(S_{\text{A,dens}}=S_A) - \nu_{\text{TEOS10}}(S_{\text{A,cond}}=S_R)$ calculated with Eq. (2) for different temperatures. The horizontal dashed line indicates the uncertainty of TEOS-10 sound speed.