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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 δw 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 δw amounts to $0.069 \pm 0.014\,\mathrm{m\,s^{-1}}$, which is 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 1 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 varying composition. Although they have been known for more than a century, these property anomalies came into focus more 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 modeling. 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 (conductivity, temperature, and pressure) measurements, according to the Practical Salinity Scale 1978 (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, has 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 $S_R = S_P\,(35.16504/35)\,\mathrm{g\,kg^{-1}}$ as the best estimate of the absolute salinity of seawater with a standard composition. Typically, δS_A in the open ocean is small but significant, reaching $\delta S_A = 0.027\,\mathrm{g\,kg^{-1}}$ 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 re-

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lated 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 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 the exact manner of sensor calibration.

We also applied one of the sensors in situ during a field campaign in the southwestern 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)[1]. The sensors are designed for in situ measurements in seawater under field conditions. They consist of a single Piezoelectric transducer/receiver and a reflector plate, which are kept at distances of 3.4 and 10 cm, respectively, by fixed rods. The time of flight is measured as a time interval of a single acoustic pulse traveling 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 the applications of equations of state (EOS). Modern digital signal processing and timing techniques provide the high resolution of the time-of-flight determination.

Table 1. Sensor specifications. The response times 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 1 (AML) and 2 years (VP), respectively (von Rohden et al., 2015).

	AML SVX	VP, VP OEM
Acoustic pathlength (mm)	68	200
Response time (µs)	$\sim$47	$\sim$140
Time resolution (ns)	$\sim$0.02	0.01
Practical resolution w (m s^{-1})	0.001	0.001
Reproducibility (m s^{-1})	0.032	0.019

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 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 (SPRTs) were placed in a sealed, well-stirred, and thermostated 55 L bath completely filled with the samples. The temperature was stabilized within $\approx$ 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 in order 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 averaged afterwards. 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

[1]Disclaimer: Any mention of commercial products within this study does not imply recommendation or endorsement by PTB.

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 2013. 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 δw is related to the salinity anomaly, we first estimated the absolute salinities S_A and the connected salinity anomaly δS for our samples. For the diluted North Atlantic water, we calculated the absolute salinity according to TEOS-10 as $S_{A,\,cond} = S_R = S_P \times u_{PS}$, 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 $S_{A,\,dens}$ 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 $1004.154 \pm 0.004\,\mathrm{kg\,m^{-3}}$. With it the absolute salinity $S_{A,\,dens}$ was calculated using the TEOS-10 expression $S_{A,\,dens}\,(T,\,p,\,\rho)$. 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 $\delta S_{A,\,m} = S_{A,\,dens} - S_{A,\,cond}$ as the measure for the salinity anomaly of the Baltic sample in $\mathrm{g\,kg^{-1}}$. 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 $S_{A,\,dens}$ as the absolute salinity described in TEOS-10, and $S_{A,\,cond}$ 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 2006–2009, and provides the basis for the calculation of the absolute salinity from knowledge of practical (or reference) salinity as the only parameter:

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

with the standard ocean salinity $S_{SO} = 35\,u_{PS} = 35.16504\,\mathrm{g\,kg^{-1}}$, and $S_R > 2\,\mathrm{g\,kg^{-1}}$.

The density of the original (not diluted) Atlantic sample was measured to $(1025.688 \pm 0.004)\,\mathrm{kg\,m^{-3}}$. 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 $0.067\,\mathrm{g\,kg^{-1}}$ agrees well with the anomaly of $0.068\,\mathrm{g\,kg^{-1}}$ calculated from Eq. (1) within the uncertainty of $0.009\,\mathrm{g\,kg^{-1}}$.

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 previously 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 (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 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 (Supplement). Within the scatter, the results from the individual sensors as a whole

Table 2. Salinity estimates for the samples used and salinity differences related to the composition anomaly for the Baltic seawater sample, including standard uncertainties.

Salinity ($g\,kg^{-1}$)	Baltic	North Atlantic	
		diluted	original
S_P/PSU	7.766 ± 0.007	7.765 ± 0.007	36.208 ± 0.01
$S_{A,\,cond}$ (assum. standard comp.)	7.803 ± 0.007	7.801 ± 0.007	36.379 ± 0.01
$S_{A,\,dens}$ (from measured density)	7.870 ± 0.006		36.381 ± 0.006
Meas. diff. $\delta S_{A,\,m} = S_{A,\,dens} - S_{A,\,cond}$	0.067 ± 0.009		
Calc. diff. $\delta S_{A,\,c}$ (Eq. 1)	0.068		

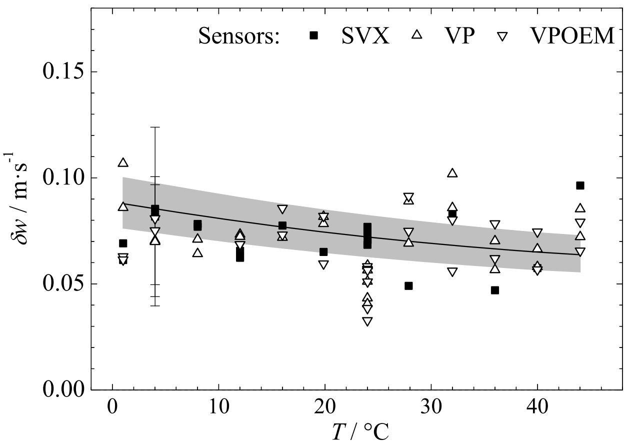

Figure 1. Speed-of-sound differences associated with the salinity anomaly for Baltic seawater at $S_P = 7.766$. Symbols: measured differences from the Baltic and the diluted Atlantic sample (NA II) with virtually the same S_P. Uncertainty bars are exemplarily given at 4 °C. Line: δw calculated as $w_{TEOS10}(S_{A,\,dens}, T, p_0) - w_{TEOS10}(S_{A,\,cond}, T, p_0)$. 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.

are indistinguishable, and no significant trend with temperature can be assessed. The average over the data points from all sensors is $\delta w = 0.069\,m\,s^{-1}$ with a standard deviation of $0.014\,m\,s^{-1}$. Note that this purely experimental estimate of δw 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 δw 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 ($S_{A,\,dens}$) and diluted Atlantic ($S_{A,\,cond}$) 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 $S_{A,\,dens}$ and would accordingly produce a virtually identical curve for δw.

2.3 Field measurements

We applied one of the sensors (VP) used for the laboratory measurements at three different sites in the southwestern 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 Sea-Bird 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 typically for 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 L 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 $2.5 \times 10^{-6}\,g\,cm^{-3}$, $k = 1$), 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).

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 1 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 dominated in most cases 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 in the anomaly effects at one site.

In the same way as described above for the laboratory investigations, we determined the salinity anomaly δS_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), δS_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 δw 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 $(w - w_{EOS})_{Baltic}$ with the analogous differences $(w - w_{EOS})_{Atlantic}$ which were calculated on the basis of laboratory records in two samples of diluted North Atlantic seawater (as a "substi-

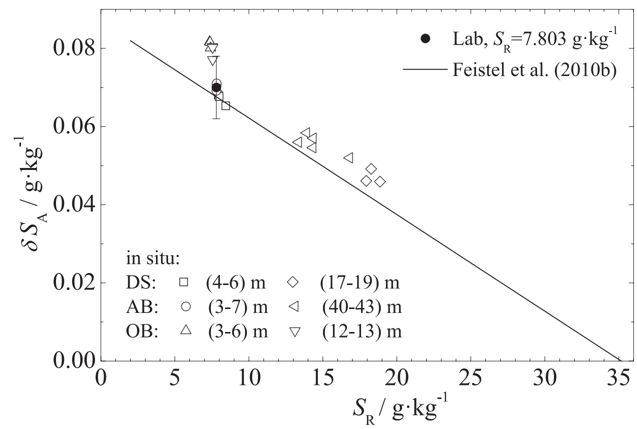

Figure 3. Salinity anomaly, determined from density and salinity measurements, vs. reference salinity $S_R = S_P \times u_{PS}$. Filled symbol: laboratory sample; open symbols: Baltic field samples. The straight line shows the parameterization of Feistel et al. (2010b), Eq. (1), for comparison.

tute" for standard seawater):

$$\delta w = (w - w_{EOS})_{Baltic,\,in\,situ} - (w - w_{EOS})_{Atlantic,\,Lab}. \quad (2)$$

The first of the reference samples is the one used for the laboratory estimate of δw 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. We classified the Baltic in situ measurements into two groups by means of salinity S_P (7.3 to 8.4, and 13.3 to 18.8). The two Atlantic reference samples can then be seen as representative of the two S_P ranges. Tables 3 and 4 are accordingly separated into upper and lower parts. The sound speed differences $(w - w_{EOS})_{Baltic}$ and $(w - w_{EOS})_{Atlantic}$ 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. However, the approach of relating the Baltic field measurements to the fixed Atlantic reference samples implies that $(w - w_{EOS})$ is virtually 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 Supplement. The results for the extracted sound speed anomaly δw are listed in Table 4 and plotted in Fig. 5. The courses of the differences $w - w_{EOS}$ reflect the inaccuracy of the sensor, with respect to absolute values, and the actual reference equation. However, due to the high sensor stability and resolution, the uncertainty of

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 δS_A based on on-board measurements.

Site	Measurements								calc. S anomaly
	In situ CTD						On-board		
	T °C	$\sigma(T)$ °C	S_P (PSU)	$\sigma(S_P)$ (PSU)	p Pa	$\sigma(p)$ Pa	ρ g cm^{-3}	S_P (PSU)	δS_A g kg^{-1}
DS	20.855	0.001	7.899	0.0009	166 308	995	1.004257	7.902	0.068
DS	21.280	0.003	7.950	0.0001	166 069	777	1.004295	7.951	0.068
DS	20.457	0.002	8.399	0.0002	144 747	246	1.004633	8.401	0.065
AB	20.995	0.001	7.773	0.0002	133 966	974	1.004162	7.775	0.069
AB	21.170	0.002	7.779	0.0002	173 492	185	1.004168	7.781	0.071
AB	21.207	0.003	7.780	0.0002	172 901	107	1.004169	7.782	0.071
OB	22.105	0.002	7.320	0.0002	134 186	813	1.003829	7.322	0.082
OB	22.007	0.001	7.344	0.0003	134 190	603	1.003846	7.345	0.082
OB	21.947	0.008	7.377	0.0033	163 016	354	1.003867	7.373	0.080
OB	20.701	0.005	7.518	0.0003	225 661	205	1.003973	7.513	0.080
OB	20.786	0.017	7.524	0.0003	225 723	190	1.003979	7.525	0.077
DS	15.192	0.001	17.849	0.0024	291 574	535	1.011767	17.846	0.046
DS	14.999	0.004	18.176	0.0044	275 119	405	1.011944	18.078	0.049
DS	14.685	0.002	18.775	0.0007	293 951	103	1.012462	18.764	0.046
AB	15.925	0.005	13.833	0.0096	503 236	153	1.008710	13.796	0.058
AB	15.081	0.002	13.293	0.0040	479 620	69	1.008288	13.241	0.056
AB	15.801	0.004	14.265	0.0039	505 692	87	1.009059	14.262	0.055
AB	15.709	0.006	14.276	0.0029	508 273	84	1.009070	14.274	0.057
AB	14.230	0.001	16.723	0.0002	531 733	405	1.010919	16.721	0.052

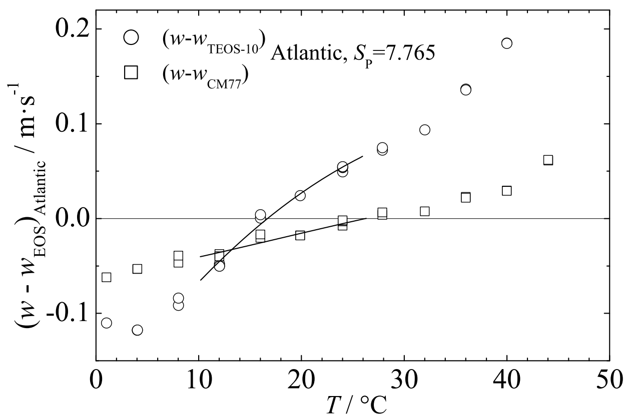

Figure 4. Time-of-flight sensor output relative to speed of sound calculated with TEOS-10 and Chen and Millero (1977) equations of state, as an example for the North Atlantic seawater sample with $S_P = 7.765$ (laboratory measurements). The lines show polynomial fits used for interpolation to extract values according to the in situ temperatures of the Baltic field measurements.

δw 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 ($\sim$ 1 week), the sensor was stable. The data show a smooth course without strong salinity dependence (Fig. 5). Especially the δw at $S_P \approx 8$ reproduce well and independently of the sample site, date, and depth (the cluster of points includes one sample from the site OB at ≈ 12.5 m).

Whereas the outputs of the equations apparently differ by $\approx 0.05\,\text{m}\,\text{s}^{-1}$ (upper panel of Fig. 5), the estimated sound speed anomaly δw is virtually 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 limited validity to oceanic salinities which do not include the brackish Baltic waters. Although a bit lower, the δw 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 δw comprise the general stability of the sensor ($0.019\,\text{m}\,\text{s}^{-1}$), represented by

Table 4. Speed of sound measured with the time-of-flight sensor in the Baltic Sea (in $\mathrm{m\,s^{-1}}$); 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. δw 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.

Site	Measured sound speed		Rel. to TEOS-10			Rel. to Chen and Millero (1977)			
			Baltic	Atlantic		Baltic	Atlantic		
	w	$\sigma(w)$	$w - w_{TEOS}$	$w - w_{TEOS}$	$\delta\omega$	$w - w_{CM77}$	$w - w_{CM77}$	$\delta\omega$	$u(\delta\omega)$
DS	1493.982	0.004	0.073	0.033	0.040	0.026	−0.013	0.039	0.033
DS	1495.284	0.005	0.081	0.036	0.045	0.032	−0.012	0.044	0.034
DS	1493.338	0.005	0.081	0.030	0.051	0.034	−0.014	0.048	0.033
AB	1494.203	0.005	0.077	0.034	0.043	0.030	−0.013	0.043	0.033
AB	1494.792	0.005	0.082	0.036	0.047	0.034	−0.012	0.047	0.033
AB	1494.907	0.009	0.090	0.036	0.055	0.042	−0.012	0.054	0.035
OB	1496.914	0.006	0.090	0.042	0.049	0.041	−0.010	0.051	0.033
OB	1496.653	0.005	0.082	0.041	0.041	0.033	−0.010	0.043	0.033
OB	1496.573	0.009	0.090	0.041	0.050	0.041	−0.010	0.052	0.041
OB	1493.218	0.010	0.088	0.032	0.056	0.041	−0.014	0.055	0.037
OB	1493.506	0.017	0.118	0.033	0.085	0.071	−0.013	0.084	0.063
DS	1487.770	0.005	0.074	−0.015	0.089	0.031	−0.053	0.084	0.048
DS	1487.476	0.007	0.070	−0.017	0.087	0.026	−0.054	0.081	0.050
DS	1487.180	0.010	0.099	−0.021	0.120	0.056	−0.057	0.113	0.049
AB	1485.888	0.013	0.053	−0.006	0.059	0.011	−0.047	0.059	0.053
AB	1482.389	0.008	0.013	−0.016	0.030	−0.021	−0.054	0.033	0.049
AB	1485.985	0.005	0.057	−0.007	0.065	0.015	−0.048	0.064	0.050
AB	1485.703	0.015	0.060	−0.009	0.069	0.018	−0.049	0.067	0.053
AB	1483.604	0.004	0.049	−0.026	0.075	0.010	−0.061	0.071	0.048

the reproducibility of calibration measurements in pure water, and the effect of conductivity (salinity), temperature, and pressure uncertainties on EOS-calculated sound speed ($< 0.04\,\mathrm{m\,s^{-1}}$). We assigned an additional contribution of $0.02\,\mathrm{m\,s^{-1}}$ 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 δw at $S_P \approx 13.3$ 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 δw 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 $\delta w = w_{TEOS}(S_A) - w_{TEOS}(S_R)$ (dotted lines in Fig. 6), where S_A and S_R are related to each other according to Eq. (2). That is, they instead follow Millero's rule (see also Fig. 13 in Feistel et al., 2010a), and therefore confirm

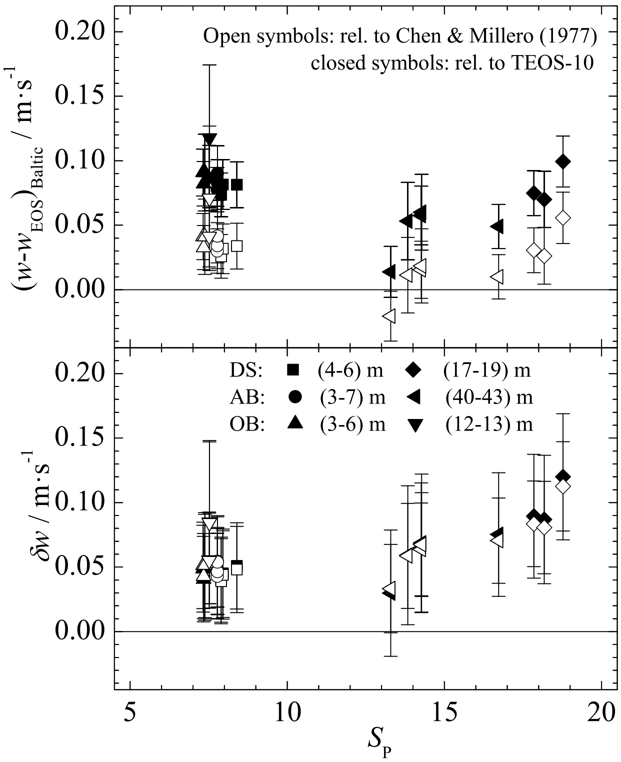

Figure 5. Upper panel: measured speed of sound (Baltic) relative to calculated values with equations of TEOS-10 and Chen and Millero (1977) for the same (S_P, T, p). The displacement between both reflects differences in the outputs of the equations. Lower panel: speed-of-sound anomaly $\delta w = (w - w_{EOS})_{\text{Baltic, in situ}} - (w - w_{EOS})_{\text{Atlantic, ref}}$ (upper panel "minus" Fig. 4).

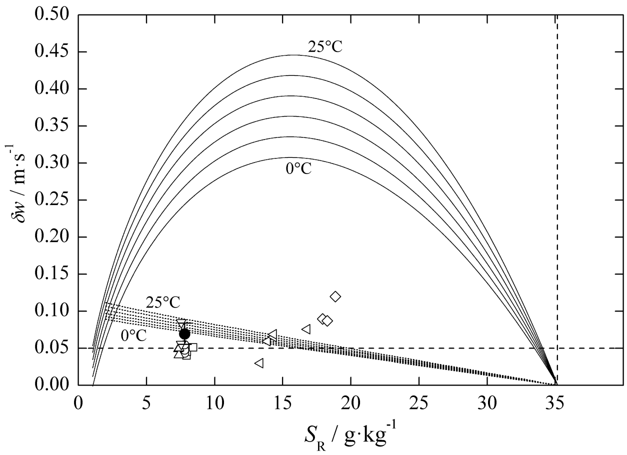

Figure 6. Experimental data for sound speed anomaly δw in Baltic seawater (symbols) in comparison to model results (curved lines, reproduced from Fig. 25 in Feistel et al., 2010a) at atmospheric pressure. Filled symbol: average of laboratory measurements in a sample with $S_R = 7.803\,\text{g kg}^{-1}$ ($S_P = 7.766$) at temperatures of 1 to 46 °C. Open symbols: data derived from off-shore measurements; see Fig. 5. The dotted lines show $\delta w = w_{\text{TEOS10}}(S_{\text{A, dens}} = S_A) - w_{\text{TEOS10}}(S_{\text{A, cond}} = S_R)$ calculated with Eq. (2) for different temperatures. The horizontal dashed line indicates the uncertainty of TEOS-10 sound speed.

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, considering the above restrictions, it is possible to give a reliable estimate of δw 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 $S_P = 7.766$ 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, non-homogeneous. That means that the anomalous salt component might be variable with respective effects on the magnitude of sound speed deviations, dependent on the timescales of the horizontal and the quite 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 in Tables 2–4 in the manuscript and in two tables in the Supplement.

The Supplement related to this article is available online at doi:10.5194/os-12-275-2016-supplement.

Author contributions. C. von Rohden designed and carried out the laboratory experiments, supervised the offshore speed-of-sound measurements, evaluated the data, and wrote the manuscript. S. Weinreben prepared the field activities and carried out the onboard density and CTD measurements. F. Fehres contributed to the data evaluation and manuscript preparation.

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