Response to RC1 (12 Sep 2017)

General comments

Thanks for the comments and questions, whose clarification contributes to the improvement of our article.

It is true that a certain amount of know-how and care is required to determine the salinity by density measurement with high accuracy. However, this know-how has been made available in this and our previous publication on our substitution method. Furthermore, it was shown in density comparison measurements, wherein oceanographic institutes were also involved, that the measuring equipment and time expenditure for a highly accurate density measurement at atmospheric pressure (in the lab) is moderate provided that the know-how is consistently applied [1].

Specific comments

Page 4 Line 1. Was the isotopic composition measured before or after degassing?

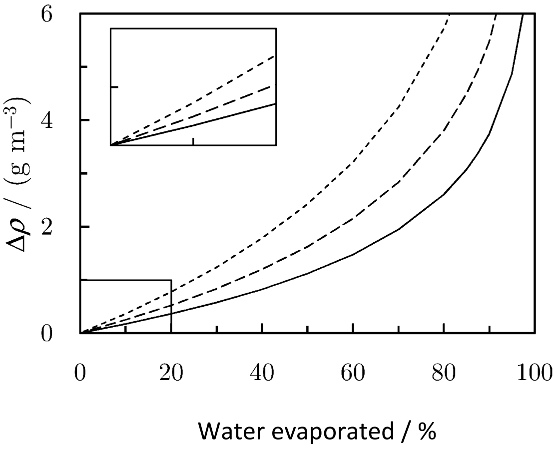
The following change was made to the manuscript (from <left> to <right>):

The isotopic abundances of deuterium and of oxygen-18 against Vienna Standard Mean Ocean Water were –59 ‰ and –8.5 ‰. Details on the determination of the air saturation and isotopic composition were given by Schmidt et al. (2016).	The isotopic abundances of deuterium and of oxygen-18 against Vienna Standard Mean Ocean Water were –59 ‰ and –8.5 ‰. The abundances were measured before and after degassing and no significant differences were found. Details on the determination of the air saturation and isotopic composition were given by Schmidt et al. (2016).

P4 L1. What amount of water can be evaporated without a significant change in the water density caused by heavy isotope enrichment?

The change in density of water caused by boiling is shown in the figure below that is based on the theoretical model described at the end. If $10\ \%$ water is evaporated, then the density increases by a maximum of $0.3\ \mathrm{g\ m^{-3}}$ suggesting that moderate boiling insignificantly enriches heavy isotopes in terms of density.

Fig. Density increase of water, $\Delta\rho$, due to isotope enrichment during boiling. Calculated curves for evaporation into a pure water vapour phase at $20\ ^\circ\mathrm{C}$ (- - -), $60\ ^\circ\mathrm{C}$ (–-–) und $100\ ^\circ\mathrm{C}$.



P7 L16–9. How was the water purified that was used to prepare the seawater samples?

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[1] Schmidt, H and Wolf, H.: Results of the Seawater Density Comparison 2014, IAPWS Annual Meeting 2015, 29th June to 3rd July 2015, Stockholm, Sweden, doi:10.13140/RG.2.2.28647.55207.

For the preparation of standard seawater (with S = 35), seawater from the North Atlantic Ocean (with S > 35) was diluted with deionized water[2]. This water is ultrapurified in a two stage process including, ia, reverse osmosis (RO), deionization (DI), UV, ion exchange, and microfiltration [3]. Such deionized water was also used for the preparation of diluted standard seawater (with S < 35) [4].

We know from own investigations of our tap water and deionized water therefrom that the isotopic composition is not changed by the ultrapurification process.

The following change was made to the manuscript (from <left> to <right>):

The water, which is ~~purified~~ and used for dilution of the natural seawater, is tap water from Havant, UK, where the supplier of the IAPSO SSW is located.	The water, which is deionized and used for dilution of the natural seawater (N. Higgs, personal communication, 2011), is tap water from Havant, UK, where the supplier of the IAPSO SSW is located.

P7 L5–6. What was VSMOW prepared from?

VSMOW was, of course, not prepared from melted ice.

The following change was made to the manuscript (from <left> to <right>):

The isotopic abundance of a water sample is usually stated relative to that of the reference material VSMOW, whose isotopic composition is based on a mixture of ocean waters ~~and melted ice~~ (IAEA, 2006).	The isotopic abundance of a water sample is usually stated relative to that of the reference material VSMOW, whose isotopic composition is based on a mixture of ocean waters (IAEA, 2006).

P19 L12–3. Which regular measurements obtained from standard seawater should be carried out in addition to density?

Dissolved silicate

It was helpful that there were published measurements of silicate in standard seawater from 1978, as these made it possible to check whether the standard seawater used for the density measurements of TEOS-10 had the same silicate content as the seawater used for our density measurements. Small amounts of dissolved silicate do not affect the conductivity significantly, but the density.

Carbon dioxide

As pointed out in the introduction of our article, CO_2 enrichment in the atmosphere will lead to CO_2 absorption into the oceans. The CO_2 content of standard seawater is promptly affected, as standard seawater is sampled close to the ocean surface and equilibrates with the atmosphere during its production over several weeks in an open vessel [2]. The change of the absolute salinity due do CO_2 absorption was modelled; it is expected that the absolute salinity will change by 0.005 until the year 2100 taking the year 2000 as reference [5]. Since part of the CO_2 contributes to the seawater conductivity, the (practical) salinity is also affected. The effect on the density–(practical) salinity relation has not been investigated, but probably should before there are any regular measurements of CO_2 absorbed in standard seawater.

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[2] Bacon, S., Culkin, F., Higgs, N., and Ridout, P.: IAPSO standard seawater: definition of the uncertainty in the calibration procedure and stability of recent batches, Journal of Atmospheric and Oceanic Technology, 24, 1785–1799, doi:10.1175/JTECH2081.1, 2007.

[3] R. Williams (Ocean Scientific International Limited), personal communication, 2017.

[4] N. Higgs (Ocean Scientific International Limited), personal communication, 2011.

[5] Woosley, R. J., Huang, F., and Millero, F. J.: Estimating absolute salinity (SA) in the world's oceans using density and composition, Deep-Sea Research I, 93, 14–20, doi:10.1016/J.DSR.2014.07.009, 2014.

If CO_2 caused inconsistencies in the density–(practical) salinity relation, regular density measurements would reveal.

Isotopic composition

The isotopic composition of near-surface seawater is usually determined by the ratio of evaporation and rainfall. The isotopic composition therefore correlates locally with salinity and temporally with season. However, taking the continuous “calving” of Greenland ice glaciers into account, which have a significantly different isotopic composition compared to seawater (as SLAP vs. VSMOW?), there might be a long-term change in the seawater isotopic composition. If this drift is measurable in standard seawater is a question of uncertainty in measurement (as it would be for measurable density changes) and mixing due to oceanic currents in terms of quantity, whereof we (as non-oceanographers) have insufficient knowledge to answer adequately.

Unkown components

A density measurement can detect a change in the seawater and is performed quickly. By contrast, a chemical analysis can identify changes, but the effort is very high. So why not combining them? If a change in density is detected, a complete (or targeted) chemical analysis identifies the cause.

P14 L34–5/P31 Fig. 10. How does the mathematical formulation of TEOS-10-density differ from that of the density–salinity relation, as this seems to cause unexpectedly large density deviations for low salinities?

In developing the density–salinity relation several mathematical formulations were considered including those with (salinity-)square-root terms, as these were used for TEOS-10 and EOS-80. However, such functions did not represent the measurement values as well as the linear terms used for the density–salinity relation.

Technical comments

Page 1 Lines 6 to 7, P1 L25–27, P19 L5–6. It should be made clearer what is meant by ‘composition’ and ‘composition change’.

The following changes were made to the manuscript (from <left> to <right>):

The determination of salinity by means of electrical conductivity relies on ~~a constant salt composition~~ in the North Atlantic Ocean, as standard seawater, which is required for salinometer calibration, is produced therefrom.	The determination of salinity by means of electrical conductivity relies on constant relative salt proportions in the North Atlantic Ocean, as standard seawater, which is required for salinometer calibration, is produced therefrom.
An unconditional prerequisite for the comparability of salinity measurements over long periods is, therefore, ~~that standard seawater has a stable chemical composition~~.	An unconditional prerequisite for the comparability of salinity measurements over long periods is, therefore, that the relative salt proportions in standard seawater are stable.
A long-term change in the ~~chemical composition of~~ seawater cannot be detected by this way as it will be overwritten by the recalibrations with actual standard seawater.	A long-term change in the relative salt proportions in seawater cannot be detected by this way as it will be overwritten by the recalibrations with actual standard seawater.

P2 L11. Replace ‘silicon’ by ‘silicate’.

The following change was made to the manuscript (from <left> to <right>):

[..] during storage, glass container material dissolves in the seawater, which is mainly ~~silicon~~ [..]	[..] during storage, glass container material dissolves in the seawater, which is mainly silicate [..]

P10 L11. Use a different word for “gassing”.

The following change was made to the manuscript (from <left> to <right>):

This temperature-dependent ~~gassing~~ is significant compared to the density measurement uncertainty.	This temperature-dependent aeration is significant compared to the density measurement uncertainty.

P12 L25. Replace ‘for safety reasons’ by ‘to be certain’.

The following change was made to the manuscript (from <left> to <right>):

Finally, the coefficients were averaged from $n =$ 15,000 runs ~~for safety reasons~~.	Finally, the coefficients were averaged from $n =$ 15,000 runs to be certain.

P16 L16. Replace ‘cylindring’ by ‘cylindrical’.

The following change was made to the manuscript (from <left> to <right>):

[..] theoretically, $F_{\mathrm{mag}} \propto \mu \cdot I$ for a ~~cylindring~~ (and circular) ring coil [..]	[..] theoretically, $F_{\mathrm{mag}} \propto \mu \cdot I$ for a cylindrical (and circular) ring coil [..]

P15 L20–1, P16 L15–6, P16 L28–9, P16 L33–4. It is not clear, who carried out the representative calculations.

The following changes were made to the manuscript (from <left> to <right>):

For this reason, the magnetic flotation method used by Millero et al. ~~was examined~~ in detail for possible issues.	For this reason, we examined in detail the magnetic flotation method used by Millero et al. for possible issues.

In order to rule out this possibility, ~~a representative calculation was carried out~~.	In order to rule out this possibility, we carried out a representative calculation.
A further representative calculation ~~was therefore carried out~~ with the values (i–iv).	We therefore carried out a further representative calculation using the values (i–iv).
~~A final calculation was performed~~ to estimate how significant the precise height positioning of the permanent magnet is [..]	We performed a final calculation to estimate how significant the precise height positioning of the permanent magnet is [..]

P26 Tab. 4 and 5. It is not obvious which equation the coefficients correspond to.

The following changes were made to the manuscript (from <left> to <right>):

Table 4. Values of the coefficients $a_{\mathrm{i,j}}$.	**Table 4.** Values of the coefficients $a_{\mathrm{i,j}}$ of Eq. (13).
Table 5. Values of the coefficients $b_{\mathrm{i,j,k}}$.	**Table 5.** Values of the coefficients $b_{\mathrm{i,j,k}}$ of Eq. (14).

Appendix: Density change due to isotope enrichment during evaporation

Isotope fractionation

If a vessel contains a very small vapour (v) compared to a liquid phase (l) each consisting of water, and the water contains ^{1}H and ^{2}H, or D, atoms and ^{16}O und ^{18}O atoms, then the frequency of these atoms in the liquid and gas phase is different. The frequency of an isotope of the liquid relative to the vapour phase is described by means of the isotopic fractionation factor α, which is for deuterium:

$$\alpha_{\mathrm{D}} = \frac{n_{\mathrm{D}}^{l}/n_{\mathrm{H}}^{l}}{n_{\mathrm{D}}^{v}/n_{\mathrm{H}}^{v}},$$

where n is the amount-of-substance. For example, n_{D}^{l} is the amount-of-substance deuterium in the liquid phase. The fractionation factor of deuterium and oxygen-18 is temperature-dependent[6].

Isotope enrichment

If a very small amount is repeatedly removed from the vapour phase at very long intervals, some molecules from the liquid phase „vaporize“ into the vapour phase at (almost) constant temperature. The infinitesimal changes in the amounts-of-substance of H and D in the liquid and vapour phase are then linked by $\mathrm{d}n_{\mathrm{D}}^{v} = -\mathrm{d}n_{\mathrm{D}}^{l}$ and $\mathrm{d}n_{\mathrm{H}}^{v} = -\mathrm{d}n_{\mathrm{H}}^{l}$. For the ratio D to H of the vapour phase, it follows that $n_{\mathrm{D}}^{v}/n_{\mathrm{H}}^{v} \approx \mathrm{d}n_{\mathrm{D}}^{l}/\mathrm{d}n_{\mathrm{H}}^{l}$. Inserting this formula into above formula, transforming and integrating from state (I) at the beginning to state (II) at the end of vaporization results in:

$$\frac{n_{\mathrm{D}}^{\mathrm{II}}}{n_{\mathrm{D}}^{\mathrm{I}}} = \sqrt[\alpha_{\mathrm{D}}]{\frac{n_{\mathrm{H}}^{\mathrm{II}}}{n_{\mathrm{H}}^{\mathrm{I}}}},$$

where all amount-of-substances refer to the liquid phase.

The isotopic composition of deuterium and oxygen-18 in water is given by isotopic abundances relative to VSMOW, δ_{D} and δ_{18}, see article. The use of the isotopic abundance instead of the amount-of-substance in above formula yields:

$$\frac{\delta_{\mathrm{D}}^{\mathrm{II}} + 1}{\delta_{\mathrm{D}}^{\mathrm{I}} + 1} = \left(\frac{n_{\mathrm{H}}^{\mathrm{II}}}{n_{\mathrm{H}}^{\mathrm{I}}}\right)^{\frac{1-\alpha_{\mathrm{D}}}{\alpha_{\mathrm{D}}}}.$$

For oxygen-18 the formula is similar.

Density change

The density change due to the enrichment of deuterium and oxygen-18 can be calculated using the formula of Girard and Menaché[7] that is given in the article’s appendix A.

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[6] Horita, J. and Wesolowksi, D. J.: Liquid-vapor fractionation of oxygen and hydrogen isotopes of water from the freezing to the critical temperature, Geochimica et Cosmochimica Acta, 58, 16, 3425–37, doi: 10.1016/0016-7037(94)90096-5, 1994.

[7] Girard, G. and Menaché, M.: Variation de la masse volumique de l’eau en fonction de sa composition isotopique, Metrologia, 7, 83–87, doi:10.1088/0026-1394/7/3/001, 1971.