Response to reviewers – RC2

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Title: Metrological concepts applied to Total Alkalinity measurements in seawater: reference materials, inter-laboratory comparison and uncertainty budget

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Dear reviewer,

We would like to greatly thank you for taking the time to review our manuscript, and giving us the opportunity to improve it thanks to your valuable comments and suggestions. We have carefully considered all your comments. You will find below how we addressed them in the revised manuscript.

The line numbers correspond to the reviewed manuscript with changes marked.

Line	**Comment**	**Response**
General comment 1	The authors do not provide uncertainty estimates for the natural seawater reference material which does not have a well-characterized reference value traceable to the SI. Although information about the trueness of the reference value is required to estimate its uncertainty, it seems that this shouldn't prevent the authors from developing a partial uncertainty budget for the open-cell titration method on natural seawater samples (similar to the uncertainty budget they presented in **Table 7**). In section 4.4, the authors discuss additional contributions that would need to be considered in an uncertainty budget for the titration of natural seawater samples. Why was this not done? Presenting an uncertainty budget for natural seawater samples would be informative to understanding the likely overall uncertainty and its most important contributions in measurements of real samples.	The uncertainty budget presented in Table 6 corresponds to the titration measurement method and the Gran's data treatment, which is also part of the determination of AT on NSW, it thus contributes to establish a partial uncertainty budget for natural samples. Estimating the uncertainty of the additional data treatment for natural seawater (NLLS regression) requires several investigation. A few of them are reported below, and presented in Sect 5.3.2 : (1) The uncertainty of practical salinity measurements (2) Possible discrepancies between total fluoride and total sulphate amount contents computed from salinity and the actual composition of natural seawaters worldwide (3) The uncertainty of dissociation constants of fluoride and sulphate ions. We agree this is highly needed and that a complete uncertainty budget for TA measurement results on natural seawater is required. However, these investigation are complex and represent a consequent amount of work, which will require, we believe, its own paper. This is presented as a perspective in the conclusion section.

General comment 2	The authors should include information about the degrees of freedom when presenting estimates of expanded uncertainties, so the level of confidence associated with the chosen coverage factor can be determined.	The level of confidence has been specified throughout the manuscript, being 95%.
General comment 3	The authors should carefully reconsider the organization of their tables. Some tables are cluttered with too much information and should be split into separate tables (or moved to the supplementary information), while others contain redundant information and should be consolidated. Some suggestions are offered in the detailed comments. The formatting of the table also makes it hard to read, as the table is cut off at the end of the page. Although the formatting will be edited in the final manuscript, for the benefit of the reviewer, the authors should ensure that each table fits onto a single page.	Tables have been reviewed and table 6 is now the combination of two former tables (6&7). It has been ensured that each table fits into a single page.
General comment 4	Many equations lack proper introduction and explanation. The authors should also carefully check the manuscript and make sure proper subscripts and superscripts are used for the various equation terms.	The manuscript has been reviewed according to this comment, and more specific comments below.
114-119	The description of the process is unclear. It sounds like a total of 35 liters of seawater was collected from various depths and filled into two containers. From those two containers, 25 liters of seawater were drawn and filled into a single container to produce a single batch of seawater. Was the seawater homogenized before filling into the two containers and/or again after filling into the 25 liter container?	The seawater was homogenized first after collection and a second time after HgCl2 addition (i.e. right before bottling). This is detailed in the preparation section.
126	"Artificial seawater" is a misnomer because the background medium is sodium chloride only without the other major seawater salts.	This has been specified in the text: "It should be noted that even if called "artificial seawater", the solution presented is made in a simple NaCl matrix, without other common seawater salts"
Table 1	Are the percent purity values listed in the table from the manufacturer or from the assay results at NMIJ and SMU? If they are assay values, they should be	They are assay values, they are now listed in a separated column. The assays can be considered as purity assessments. For NaHCO3 the

	listed in a separate column or a separate table rather than in parentheses after the manufacturer name. What are the likely impurities in the salts, and were the impurities assessed?	assay is made in base amount content, which can be higher to 100% due to decomposition of the salt.
Table 1 & 3	Two batches of artificial RM were produced, yet Table 1 only lists amount contents and molalities for one batch. Which batch do these values refer to? Also consider combining Table 1 with Table 3. The background alkalinity of the NaCl should also be explicitly listed in the consolidated table.	The composition given in Table 1 indicates the targeted composition. This has been specified in the text. We believe the targeted composition should remain in the method section while the table 3 contains results, especially the reference value of artificial solutions. The background Alkalinity has been added in this table.
129, table 1	The use of pHT may not be appropriate in a NaCl medium as it does not contain sulfate. The temperature and dissociation constants used to calculate pH should also be given. The text indicates that the pH was estimated roughly based on a Bjerrum plot. The authors should provide a more precisely calculated value (especially if listing the pH in Table 1) or exclude the information about pH altogether, as it isn't strictly necessary to report for this reference material.	As in Wolf-Gadrow et al (2007), the stoichiometric pK values ($pK*$) typical for seawater were used here for the simple system, at 25°C. We agree the information about pH is not strictly needed for the material, we thus removed the detailed information from table 1 and from the text, only mentioning that we chose to approach a pH close to the one of seawater.
167	"Material described in Appendix B" – Is this referring to the HCl standardized at SMU? Please state explicitly to avoid confusion and reference Appendix B for the details.	It refers to the entire materials and devices presented in Appendix B.
422-425	indicates the possibility of background alkalinity in the other salts such as NaHCO3 and Na2CO3. Was this assessed?	As both NaHCO3 and Na2CO3 have been characterized by coulometry at NMIJ in term of base amount content, no additional background alkalinity should exist in these salts. This has been added in the discussion section 3.3.2.
422-425	What would be the intercept in Fig. 2 if the linear regression was not forced to zero? Might the choice to force the regression to zero discard information about the background alkalinity from the NaHCO3 and Na2CO3?	The intercept would be 1.96 µmol.kg -1. As both NaHCO3 and Na2CO3 have been characterized by coulometry at NMIJ in term of base amount content, no additional background alkalinity should exist in these salts. This has been added in the discussion section 3.3.2.
202-204, Table 3	"Means of standard deviation" – If pooling standard deviations with uniform sample sizes, it should be calculated as the square root of the mean of the variances.	The manuscript and the values have been corrected accordingly.

216	Change phrasing to “ratio of the slope to the standard deviation of the slope.” Also consider changing the notation so that the Student’s t-value is not confused with t for time. α and 0 should be in subscripts. This comment also applies to Table 4.	The manuscript has been corrected accordingly. The notation of the time in equations 12 and 13 has been slightly modified to avoid confusion.
Equ 8, l.248	Aren’t the salts added as stock solutions? In this case, Eq. 8 should have mstock instead of msalt . mtotal should be the sum of the stock solutions plus additional water rather than the sum of the salts and water.	The manuscript has been corrected accordingly.
280	“To maximize the uncertainty of the slope” suggests that the goal was to have a larger uncertainty. I think what was meant was that the first approach with the larger uncertainty estimate was selected as the more conservative estimate of the uncertainty of the slope.	Yes, this has been more clearly specified in the text.
Equation 11, l.288-302	The equation for the homogeneity uncertainty does not make sense to me. It appears to be a standard deviation of the mean, but if so, it should be s / . However, this would not make sense either as the between-bottle variability was estimated differently for the different batches—some batches using the standard deviation of single measurements from different bottles and another batch using the standard deviation of the bottle means from repeatability measurements. It also does not make sense why the within-bottle homogeneity was neglected in the overall homogeneity uncertainty, as the within-bottle homogeneity was explicitly estimated and listed in Table 4. The observed between bottle variance should be a sum of the within bottle variance and the homogeneity variance. If the between bottle variance is calculated as the standard deviation of the means from repeatability measurements in different bottles, then $s_{obs,bet-btl} = \sqrt{u_{\text{hom}}^2 + \frac{s_{repeatability}^2}{n}}$ where n is the number of repeatability measurements within a single bottle.	The equation 11 has been reviewed as $u_{hom} = \sqrt{(M_{between} - M_{within})/\, n0}$ following ISO 33405. Details on the computation of this value have been added to the text.

	As the other reviewer noted, the within and between bottle homogeneity components can be evaluated with ANOVA according to ISO Guide 35. It would be beneficial for many readers who do not have access to the ISO documents to derive these equations at a high level.	
Equation 12 and 13, l.305-311	The equations for the stability uncertainty require more explanation for the reader. Two equations are used. In the case of no significant trend, the stability uncertainty only has one contribution from the uncertainty of the slope b1, while for cases with significant trends, the stability uncertainty has an additional rectangular distribution component. Also, what value is used for time t? And as noted before, this notation can be confused with the Student's t value.	The added term in equation 13 corresponds to the estimated degradation of the material, this has been specified in the text. A subscript has also been added to the term t (t_m) so that it cannot be confused with the Student's value. The value used for t_m is 3 months.
530	The phrasing in this sentence is confusing. The median of the set of means (from repeatability measurements made by each participant) was calculated for two different materials—natural seawater and the artificial RM (Batch 1).	The manuscript has been corrected accordingly.
545	I recommend replacing "samples" with "materials" to be clear that it was two different materials being analyzed and not two bottles.	The manuscript has been corrected accordingly.
551	How is the mean $(X_l - Y_l)$ calculated? Is it the mean difference from the 5 participants? Please clarify in the text. Why does the mean have a different subscript *l* instead of *i*, and what does it indicate?	Yes, the text has been clarified and the typo error has been corrected to make notations consistent.
619-622, Equ 16	There seems to be missing text that should precede this equation. The text following the equation states that s_r is the intra-laboratory standard deviation divided by the square root of the mean number of replicates – this should be explicitly written in the equation.	The manuscript has been corrected accordingly.
628-639	Both of these equations need proper introduction for the reader. They are based on the equations in ISO 21748. As some readers may not have access to the ISO documents, it would be helpful	Precisions from the ISO and for the calculation of s_L and s_r have been added. $u(\hat{\mu})$ has been replaced by u_{RM} to be consistent with equation 6.

	to provide an explanation of these equations and how the inter and intra-laboratory standard deviations are calculated. The term $u(\hat{\mu})$ needs further explanation than simply "standard deviation of the certified reference value." It is the uncertainty of the reference value which includes contributions from the characterization of the salts, the homogeneity, and stability (**Equation 6**). The notation should be revised so that it is consistent with **Equation 6.**	
Table 3, 336	The organization of this table is very confusing. Some entries are standard uncertainties with units of μmol kg^{-1}, while others are not. The caption indicates all numerical values have units of μmol kg^{-1}, but this is not true for parameters such as the slope, slope standard deviation, and Student *t* values. The stability uncertainty (from **Equation 12** and **13**) are not listed in this table. At the very least, the authors should clearly indicate in the table which parameters are standard uncertainties and include the appropriate units for each parameter. A better approach, I think, is to limit the table to only one type of information (e.g., the standard uncertainties associated with homogeneity, stability over time, and stability to transport). Additional details on the stability evaluation (e.g., the slope, *t*-tests, etc.) can be described in a separate table. The authors could also consider combining the information on the homogeneity and stability uncertainties from **Table 4** and **Table 5,** although the natural seawater reference material does not have a certified value and an associated uncertainty	The units have been corrected in the table, as well as indication of standard deviations values. Table 3 gives the results of the stability and homogeneity tests while table 4 gives the uncertainty values. To make the distinction clearer, two sub-sections have been made.
Table 4	Although Equation 11 will need to be revised, I will point out that the values listed for the homogeneity uncertainty do not agree with Equation 11 if using the between bottle standard deviations in Table 4 as s and N = 3. The authors should check their calculations in the tables.	The between-bottle standard deviation was noted as s^2 in the former equation 11. Using the between bottle standard deviations in Table 4 as s^2 and N = 3 allows to get the correct u_{hom} values reported. Although the equation 11 has indeed now been reviewed.

585	S_R is the reproducibility standard deviation. This term should be introduced and defined much earlier in Section 2.4.1, where it is used in Equation 16.	Only s_r, the intra-laboratory standard deviation, is used in equation 15 and 16, where it is defined.
585	Replace "precision" with "reproducibility standard deviation" to be clear what quantity is being reported. The term "precision" should be reserved for qualitative descriptions. It may also be informative to report the reproducibility standard deviation excluding Laboratory 1, as their measurements were discovered to have a systematic error due to malfunctioning of the titrant delivery on their measurement system.	Precision is defined in the VIM as the "closeness of agreement between […] measured quantity values obtained by replicate measurements on the same or similar objects under specified conditions", it is "expressed numerically by measures of imprecision, such as standard deviation". As indicated in the manuscript, the precision of the method is given by the computation of s_L and s_r, being, respectively, inter and intra laboratory variation. Laboratory 1 is already excluded from the calculation (line 561).
Table 5	The numeric values should not be left in E+00 notation form The units also need to be specified for the standard uncertainties.	The manuscript has been changed accordingly.
Section 5.3	This section deserves more discussion of the results rather than just a description of the data contained in **Table 6** and **Table 7.** Consider splitting this section into two—one discussing the top-down uncertainty estimates and the other discussing the bottom-up estimates.	With the restructuration of the article suggested by reviewer 1, the discussion about the uncertainty estimate results now comes right after the result section, it has been splitted in accordance with your comment.
Table 6, l.690-692	The formatting of this table needs much reworking to improve readability. The last column lists the individual standard uncertainties for the sub-sources of uncertainty and a combined standard uncertainty for the input parameter all in the same column. These should be separate columns. Other information is also needed such as the sensitivity coefficients used in the uncertainty propagation, and the degrees of freedom for each uncertainty contribution. Consider including a more condensed table of the uncertainty budget in the main manuscript and a more detailed version in the supplementary information.	Table 6 has been reviewed accordingly. Tables have been added in Appendix D with details on the uncertainty propagation, integrating sensitivity coefficients.

119-121, 145-148 & 491.	This section discussed leaching of silicate from the borosilicate glass bottles as a potential cause for instability in some batches of reference material. It would be beneficial for other reference material producers and for future investigations to provide more details on the specifications of the borosilicate glass used (such as the manufacturer and coefficient of linear expansion of the glass), as well as any cleaning procedures performed before bottling. Were the bottles cleaned in any way? **Line 140** states that Schott borosilicate bottles were used for Batch 2 of the artificial reference material. What about the other batches?	Other batches were bottled in Pyrex bottles, which may explain the difference observe in the amount of silicate release (although all bottles were borosilicate 3.3, i.e. same thermal expansion coefficient). This information has been added in the manuscript (Sect 3.3.4 and 3.1.1). The cleaning treatment has been specified.
740	This figure is rather confusing and not very informative. Although it highlights some major sources uncertainty such as the measured potential and the volume of acid delivered, it doesn't include all the sources of uncertainty in **Table 7** and their magnitudes. A bar graph providing a visual summary of **Table 7** may be a better choice.	It doesn't include all the sources of uncertainties as the remaining sources are highly negligible and would not appear either on this diagram nor on a bar graph. This precision has been added to the text.
Equation A.2	The total hydrogen ion concentration $[H^+]_T$ on the total pH scale includes free hydrogen ions and bisulfate ions only (Dickson, 1993). $[H^+] + [HSO_4^-] + [HF]$ is the total hydrogen ion concentration on the ***seawater*** pH scale. The notation should be revised in this equation.	The equation is written as follows: $[H^+] + [HSO_4^-] + [HF] \approx [H^+]_T$ i.e. as approximately equal to the total hydrogen scale, as indeed, this doesn't include fluoride ions, which can be neglected here.