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Modelling organic alkalinity in the Baltic Sea using a Humic-Pitzer approach

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Abstract

Significant excess alkalinity, of the order of 30 μmol kg^{-1} and attributed to dissolved organic matter, has recently been measured in the Baltic Sea. Chemical speciation modelling shows that the measured excess alkalinity is consistent with an organic alkalinity derived from dissolved organic carbon, assuming that this dissolved organic carbon consists entirely of terrestrial humic substances. The contribution of polydisperse material such as humic substances to titration alkalinity invalidates the assumptions on which the current definition of titration alkalinity is based. It is therefore concluded that alkalinity should currently not be one of the parameters used to characterise the CO_2 system in organic-rich waters. The use of a simple relationship to estimate organic alkalinity from the dissolved organic carbon concentration is assessed for the limited Baltic Sea data set currently available.

1. Introduction

The carbon dioxide system in marine waters is described by four parameters, where measurement of any two allows the other two be calculated. The four parameters are total inorganic carbon (*DIC*), pH, fugacity or partial pressure of carbon dioxide ($f\mathrm{CO}_2$ or $p\mathrm{CO}_2$) and total alkalinity (*TA*). Of these parameters, *DIC*, pH and $f\mathrm{CO}_2$ have unequivocal chemical definitions, while *TA* has an open-ended definition: *"The total alkalinity of a natural water is thus defined as the number of moles of hydrogen ion equivalent to the excess of proton acceptors (bases formed from weak acids with a dissociation constant $K \leq 10^{-4.5}$, at 25°C and zero ionic strength) over proton donors (acids with $K > 10^{-4.5}$) in one kilogram of sample"* (Dickson, 1981). This leads to the following equation:

$$TA = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [SiO(OH)_3^-] + [NH_3] + [HS^-] + \cdots - [H^+]_F - [HSO_4^-] - [HF] - [H_3PO_4] - \cdots \qquad (1)$$

where the ellipses denote unknown protolytes. Dickson's definition takes advantage of the fact that there are no inorganic components with pK (=-$\log_{10}K$) values close to the limit of 4.5. The nearest are the dissociation of carbonic acid to bicarbonate (pK = 6.36 at 25°C and zero ionic strength) and the dissociation of hydrofluoric acid to fluoride (pK = 3.17 at 25°C and zero ionic strength). Titration of a seawater sample with strong acid therefore provides a natural endpoint following the protonation of bicarbonate, where the number of moles of added acid is equal to number of moles of alkalinity in the sample. This is, however, an operational measurement that relies on the absence of proton exchange reactions in the region around pH 4.5.

There are a number of reports in the literature of excess alkalinity, i.e., alkalinity over and above that which can be explained by Equation (1) following measurements of two or three of the other CO_2 system parameters. (e.g., Kim et al., 2006; Kim and Lee, 2009; Hunt et al., 2011; Koeve and Oschlies, 2012). This excess alkalinity is interpreted as organic alkalinity, i.e., that weak organic acids also contribute to the value of *TA* in Equation (1). Extension of Equation (1) to include organic acids is not easily achieved where the nature of the organic acids is not known: in estuarine and near-shore waters, terrestrial humic substances are considered to contribute significantly to the dissolved organic matter (Cai et al., 1998).

Humic substances in dissolved organic matter are divided operationally into two fractions: fulvic acid (FA) and humic acid (HA), where FA has a significantly lower median molecular weight. Both fractions are polydisperse, i.e., consist of moieties covering a significant range of sizes and chemical properties. In this case, the most significant aspect of polydispersity concerns acid-base properties (pK values): humic substances show a continuum of pK values in the pH range 2 to 10. Inclusion of humic substances would therefore invalidate the assumption behind Equation (1), that no proton exchange reactions are occurring in the region of the titration endpoint at pH ≈ 4.5.

The Baltic Sea is an ideal area for examining the potential contribution of humic substances to measured total alkalinity. The brackish surface water contains relatively high concentrations of dissolved organic matter, and fluorescence measurements indicate significant concentrations of humic substances (Skoog et al., 2011). Kulinski et al (2014) have recently reported measurements of organic alkalinity in the Baltic Sea. We use these data, together with chemical speciation modelling, to examine the consequences of humic substances for the determination and interpretation of total alkalinity and its organic component.

2. Theory

2.1 Humic ion-binding model

Freshwater chemists have carried out extensive studies of the proton exchange and metal binding properties of humic substances extracted from different water bodies. These have formed the basis for the development of two generic models for humic substance chemistry: WHAM (Tipping et al., 2011) and NICA-Donnan (Kinniburgh et al., 1996; Koopal et al., 2005). WHAM models the polydisperse nature of the humic substances using a combination of discrete binding sites, where the binding strength for protons and metal ions is modified by the charge developed on the humic "molecule". The NICA-Donnan approach, in contrast, describes the binding strength in terms of distribution curves of binding strengths, again modified by the development of charge. Parameters for both models have been obtained for the FA and HA fractions by fitting to a wide range of experimental data, and the two models give broadly comparable results (Ge et al., 2005). In this work we have used the WHAM formulation (Model VII) to represent the natural organic matter in the Baltic Sea. Figure 1 shows typical modelled distributions of proton binding strength in Baltic Sea water, where the effect of binding by calcium and magnesium has been taken into account. The binding strength is expressed as the derivative of the number of bound protons against pH, dn/dpH: the area under the curve in a given pH range thus represents the number of protons that are exchanged with organic matter over that pH range.

2.2 Pitzer equations

The Pitzer specific ionic interaction model (Pitzer, 1991) is one of the most widely used specific interaction models in order to account for non-ideal behaviour of electrolytes due to ionic interactions, such as in the seawater ionic medium (Harvie et al., 1984; Millero and Pierrot, 1998). It treats strong electrolytes as completely dissociated, and the properties of the solutions are described as far as possible in terms of interactions between free ions, in contrast to the ion-pairing model (Dickson and Whitfield, 1981).

The Pitzer model is based on an extension of the Debye-Hückel theory using a virial equation approach. The general form of the Pitzer equations for estimating the single-ion activity coefficients is given by

$$\ln \gamma_i = f^{\gamma} + \sum_{ij} m_i m_j B_{ij} + \sum_{ijk} m_i m_j m_k C_{ijk} \qquad (2)$$

where f^{γ} is a Debye-Hückel term that accounts for long-range interactions, B_{ij} is a coefficient related to binary interactions of all the components (plus-minus, plus-plus and minus-minus), and C_{ijk} is related to ternary interactions of all the components (plus-minus-plus, plus-minus-minus and minus-plus-plus). These interaction coefficients include semi-empirical Pitzer parameters which are linear combinations of ion and solvent specific parameters. The Pitzer parameters used in this work are based on the modified MIAMI Ionic Interaction Model (Waters and Millero, 2013).

The calculation programme GIVAKT used for this work combines Pitzer equations for the dissolved phase with the WHAM VII equations for humic substances. GIVAKT uses the optimization algorithm developed for HALTAFALL (Ingri et al., 1967), implemented in Excel Visual Basic. This algorithm, although not the fastest, has the advantage that it converges irrespective of the values of the initial guesses. This is, to our knowledge, the first complete combination of a Pitzer model with a humic substance model. A previous combination of Pitzer equations with WHAM VI, implemented in PHREEQC (Parkhurst and Appelo, 2013), required some modification to the charge dependence of WHAM binding constants, in order to fit within the confines of the PHREEQC formulation (Liu et al., 2008; Marsac et al., 2011).

2.3 Evaluation procedures for total alkalinity

The two most common, or recommended, methods to estimate *TA* and *DIC* from potentiometric titration data are (i) the modified (or extended) Gran function (Hansson and Jagner, 1973; Grasshoff et al., 1999) where the equations below are rearranged to a linear form and then fitted iteratively by least-squares and (ii) the use of a non-linear least-squares approach that fits a model curve to the titration curve based on the experimental parameters acid volume (Johansson and Wedborg, 1982) or the electromotive force (emf; potential) (Dickson, 1981; Dickson et al., 2007).

Relative to the proton condition from the definition of *TA* in Equation (1), the analytical total concentration of hydrogen ion (H_{TOT}) is, at any point in the titration, given by (Dickson et al., 2007):

$$\mathrm{H_{TOT}} = [\mathrm{H^+}]_\mathrm{F} + [\mathrm{HSO_4^-}] + [\mathrm{HF}] + [\mathrm{H_3PO_4}] - [\mathrm{HCO_3^-}] - 2[\mathrm{CO_3^{2-}}] - [\mathrm{B(OH)_4^-}] - [\mathrm{OH^-}] - [\mathrm{HPO_4^{2-}}] - 2[\mathrm{PO_4^{3-}}] - [\mathrm{SiO(OH)_3^-}] - [\mathrm{NH_3}] - [\mathrm{HS^-}] \quad (3)$$

The initial analytical total concentration of hydrogen ion in the solution is thus the negative of the alkalinity, i.e., $H_{TOT} = -TA$. The total concentration of hydrogen ion can also, at any point in the titration be described by the mass (m) and concentration (C) of the added acid, the initial total amount of hydrogen ion (m_0TA) and the total sample mass ($m_0 + m$), resulting in the equation:

$$\frac{mC-m_0TA}{m_0+m} = [\mathrm{H}^+]_\mathrm{F} + [\mathrm{HSO}_4^-] + [\mathrm{HF}] + [\mathrm{H}_3\mathrm{PO}_4] - [\mathrm{HCO}_3^-] - 2[\mathrm{CO}_3^{2-}] - [\mathrm{B(OH)}_4^-] - [\mathrm{OH}^-] - [\mathrm{HPO}_4^{2-}] - 2[\mathrm{PO}_4^{3-}] - [\mathrm{SiO(OH)}_3^-] - [\mathrm{NH}_3] - [\mathrm{HS}^-] \qquad (4)$$

The Nernst equation is used together with Equations (3) and (4) to relate the emf of the pH cell to the total concentration of hydrogen ion. Furthermore, salinity- and temperature-dependent relationships that express the individual species concentrations in terms of total concentrations and the appropriate dissociation constants are applied (Dickson et al., 2007). Equations (3) and (4) are the basis for both the modified Gran function and the non-linear curve fitting approach, but their complexity may differ depending on the application.

Other methods have also been used to evaluate *TA* from potentiometric data. Haraldsson et al. (1997) used a titration procedure with a five-point non-modified Gran function, positioning the data points in such a way as to minimize the contribution of side reaction with sulphate and fluoride. The method of the difference derivative of pH as a function of added acid volume (Hernández-Ayón et al., 1999; Hernández-Ayón et al., 2007; Muller and Bleie, 2008), has been used to identify the contribution of excess organic alkalinity. The methods involves plotting of the dpH/dV of the titration curve against acid volume, and a sharp slope maximum at the second inflection point is obtained from which the equivalence volume can be determined by simple computational techniques.

3. Data and methods

3.1 Description of data

The data used in this work are based on a recent report on the contribution of organic alkalinity in the Baltic Sea (Kuliński et al., 2014). Six stations (Table 1) were chosen based on the availability of measurements of dissolved organic carbon (DOC) over the salinity range 3-8. Measurements of the four master parameters, TA, DIC, $\mathrm{pH_{tot}}^{25}$, and $p\mathrm{CO_2}$, provided a fully overdetermined CO_2 system. TA was determined by potentiometric titration (0.1 m HCl, ρ=1.00142 g $\mathrm{cm^{-3}}$), in a VINDTA system (Versatile INstrument for the Determination of Titration Alkalinity, produced by Dr. Ludger Mintrop, MARIANDA, Kiel, Germany). The reported TA was evaluated by non-linear curve fitting within the VINDTA LabView-software and accuracy was assured using Certified Reference Materials (CRM) provided by A. G. Dickson, Scripps Institution of Oceanography, USA. The contribution of organic alkalinity was determined as the excess alkalinity given by the difference between measured TA and TA calculated from DIC and either pH (A_{org-1}) or $p\mathrm{CO_2}$ (A_{org-2}).

It should be noted that, following re-evaluation of the raw data, TA in Table 1 of Kulinski et al. (2014) should read 1648, 1624, 1625, 1624 µmol $\mathrm{kg^{-1}}$ for stations 5, 6, 7, and 8, respectively, with corresponding changes in the determined A_{org} (stations 6 and 7 are not included in Table 1 of this paper since they lack DOC measurements). This has also a small effect on their estimated bulk dissociation constant of dissolved organic matter, $\mathrm{p}K_{\mathrm{DOM}}$ and the fraction f of DOC that acts as a carrier of weak acidic groups (see section 4.5). Hence, we use the corrected values for stations 5 and 8 in this study (Table 1).

3.2 Modelling of theoretical titration curves

Theoretical titration curves of seawater are provided by GIVAKT by converting the resulting free proton concentration into potentials (emf) according to the Nernst equation:

$$E \; = E° + RT\ln([\mathrm{H}^+])/F \qquad (5)$$

where E is the potential, $E°$ is the standard potential of the system (electrode), R is the gas constant (8.31451 J mol^{-1} K^{-1}), T is the temperature in Kelvin, and F is the Faraday constant (96 485.309 C mol^{-1}). The potential E is then used in the evaluation methods (Sections 2.3 and 3.3). The standard potential $E°$ can be somewhat arbitrarily chosen (typically 300-600 mV) since it is iteratively optimized during the evaluation procedure (Section 3.3). For organic-free water samples, the total concentration $\mathrm{H}_{\mathrm{TOT}}$ of the hydrogen ion in GIVAKT is equal to $-TA$.

The model titrations are based on the data given in Table 1, and were set up as follows. For each station, the total hydrogen ion concentration $\mathrm{H}_{\mathrm{TOT}}$ is first calculated using the sample's pH and *DIC*, and the appropriate concentration of humic substances. This $\mathrm{H}_{\mathrm{TOT}}$ is then used together with a constant *DIC* to simulate a closed-cell titration (cf. Dickson et al., 2007). The free proton concentration is converted to potential according to Equation (5).

3.3 Description of evaluation methods

In this study, we use the MATLAB program 'VINDTA_CALCALK' that calculates the total alkalinity and various associated parameters of a seawater sample using titration data obtained using a VINDTA system. The program has a long history, originally being a QuickBasic script written by Ernie Lewis (1997). That code, adopted and adapted by Ludger Mintrop (2003) was the basis for both the VINDTA's own LabView-software and a MATLAB-translation by Dorothee Bakker (2006). This code was optimised by Steven van Heuven in 2008. After being fed the input data, the program uses an iterative Gran approach to determine an approximate state of the carbonate system that, within boundary conditions prescribed by the user's input, predicts as well as possible the titration results obtained (and input) by the user. This is the *Gran optimisation* result (Figures 2 and 3). After that step, a further refinement of the assumed state of the carbonate system is obtained by an iterative 'chi-square' (χ^2) function. This gives the χ^2 *optimsation* result (Figures 2 and 3).

Additionaly, in this study, a non-linear curve fitting method using the Levenberg-Marquardt algorithm was included in the program following the FORTRAN 77 (F77) program as referred to in the SOP3a (Annexe 1) in Dickson et al. (2007), giving the *non-linear* result (Figures 2 and 3). *TA* is one of the optimised parameters of the carbonate system and is output to the user, together with *DIC*, the electrode's standard potential $E°$, and the first dissociation constant of carbonic acid, K_1*. It should be noted that the VINDTA LabView-software uses the results of the Gran optimisation as input parameters for the non-linear curve fitting which fits the acid volume to the titration curve. This in contrast to the non-linear curve fitting in the MATLAB program which uses stand-alone input parameters and fits the potential (emf) to the titration curve. The latter involves equations of higher order compared to a linear equation with respect to volume. Although differences in *TA*, depending on the choice of dependent variable, are negligble for theoretical titrations, analytical uncertainties in the these experimental variables can be important and differences on the order of 1-3 μmol kg^{-1} in *TA* have been reported (Johansson and Wedborg, 1982).

For the titration data generated by GIVAKT, a modified Gran method using bicarbonate concentrations from GIVAKT was also used as an evaluation method, giving the *Gran F2'* result (Figure 4).

3.4 Tests of the evaluation methods

The different evaluation methods in the MATLAB routine were tested for performance using (i) the seawater titration data given in the iterative non-linear curve fitting F77 program referred to in Dickson et al. (2007) (test data); and (ii) the corresponding modelled titration data provided by GIVAKT (model data). The residuals in *TA* for the different methods are shown in Figure 2 and the fitted parameters are listed in Table 2. The evaluation methods are in good agreement with the default data for both data sets with respect to *TA* and the other fitted parameters. The effect of using different dissociation constants in the non-linear evaluation method for the conditions of the default titration data is of minor importance with mean standard deviations of 0.05 and 0.06 µmol kg^{-1} for the test and model titrations, respectively. Accordingly, the constants of Dickson et al. (2007) were used for the test data and Mojica Prieto and Millero (2002) for the field data. The precision for the non-linear method was found to be 0.35 µmol kg^{-1} for the modelled titration curves over a wide salinity range (3-35). It should be noted that the Pitzer parameters used in GIVAKT provide a slightly different $\mathrm{p}K_1^*$ than in the test titration data given by Dickson et al. (2007).

4. Results and discussion

In this work, we have explored the possibility of using a humic ion-binding model coupled to a specific ion interaction (Pitzer) model to explain the contribution of organic alkalinity in the Baltic Sea as reported in a recent study by Kuliński et al. (2014). We have investigated the meaning of alkalinity for a polydisperse material that ionises over a wide pH range and also explored the consequences for the measurement and interpretation of organic alkalinity by conventional evaluation methods.

4.1 Titrations of Baltic seawater including fulvic acid

Raw analytical data from titrations of organic-rich Baltic seawater (Table 1) were re-analysed by different evaluation methods and corresponding theoretical titration data were generated with the inclusion of humic substances in the form of FA. Initial model runs showed that, in order to match the measured *TA* for most stations in Table 1, the mass of FA present needed to be twice the mass of organic carbon, i.e., [FA]/µg L^{-1} = 2 * [DOC]/µg L^{-1}. If the DOC consists entirely of FA, then this result is consistent with the estimate of Tipping (2002) that the concentration of active humic matter is less than or equal to twice the DOC concentration, since humic matter is about 50% carbon by weight. We therefore set the mass concentration of FA to twice that of DOC in the following calculations.

Analysis of field and model titrations are exemplified by residuals in *TA* of data from Station 3 (Table 1) shown in Figure 3 and the fitted parameters are listed in Table 3. These residuals are larger and more variable than in the test titrations (Figure 2). This was most apparent near the equivalence volume (here ≈ 1.7 mL), resulting in larger uncertainties in the estimated *TA*, as well as in the other fitted parameters. Despite this, there is a general agreement between the different evaluation methods for the practical and theoretical titrations.

4.2 Measured and modelled organic alkalinity

The modelled titrations were compared to the results of Kuliński et al. (2014) (Table 1). The contribution of organic alkalinity (A_{org}) was estimated as the difference between the modelled *TA* determined by the different evaluation methods and the inorganic alkalinity calculated using GIVAKT (Figure 4). There was significant scatter in the data from the different evaluation methods, with larger deviations at higher DOC concentrations. The modified Gran function (F2′) was based on bicarbonate concentrations calculated by GIVAKT. Additionally, A_{org} was estimated as the difference between the measured *TA* by Kuliński et al. (2014) and the inorganic alkalinity as given by the model, i.e., not dependent on the identification of the equivalence point by different evaluation methods of the modelled data. These data (filled diamonds in Figure 4) were in excellent agreement with the measured concentrations of A_{org}, which is expected if the inorganic alkalinity provided by GIVAKT truly reflects the carbonate-based *TA*, as calculated from measured *DIC* and either pH or $p\mathrm{CO}_2$ according to Kuliński et al. (2014).

Should *TA* be overestimated due to excess alkalinity within the model, the apparent higher concentration of *TA* will depress the calculated value of $p\mathrm{CO_2}$. However, there was good agreement between modelled and measured $p\mathrm{CO_2}$ for most stations (Figure 5).

4.3 Interpretation of the measured organic alkalinity

Although the *TA* values obtained from the field data and the corresponding GIVAKT calculations are in good agreement, the corresponding estimates of organic alkalinity do not correspond to Dickson's definition. Figure 6 shows the difference derivative of the charge of fulvic acid as a function of pH (dn/dpH). The total area below the dn/dpH curve corresponds to the total concentration of ionisable sites as defined by WHAM VII. The area below the dn/dpH curve between the initial sample pH (~8.0) and the pH at the equivalence point (~4.4) should, according to Dickson's definition, correspond to the contribution of organic alkalinity to the measured *TA*.However, additional excess organic alkalinity as indicated by the lower equivalence point pH (~2.8) is needed in order to match the *TA* determined from conventional evaluation methods (Figure 6). It should be noted here that the various evaluation methods assume that the acid-base chemistry occurring after the titration endpoint can be described by the inorganic components of seawater: with FA present this is clearly not the case, since protonation of FA continues beyond the endpoint. The over-estimation of organic alkalinity thus appears to be a result of an incomplete description of the sample chemistry during the titration.

The difference derivative of pH as a function of acid volume (dpH/dV), proposed as an evaluation method by Hernández-Ayón et al. (2007) is shown in Figure 7 for two different samples of salinities 35 and 10 with different amounts of fulvic acid added (0, 5, 10 mg FA $\mathrm{L^{-1}}$). The addition of excess organic alkalinity in the form of polydisperse humic material obviously requires a larger equivalence volume, but it also distorts the curve after the equivalence point. Offsets in equivalence volume as determined by the Hernández-Ayón et al. (2007) method (dpH/dV) corresponds to the excess organic alkalinity determined from the dn/dpH curve between the initial sample pH and the pH at the equivalence point.

4.4 Practical implications: alkalinity as a conservative property

For experimentalists who wish to characterise the CO_2 system, the implications from this work are clear: titration alkalinity should not be one of the parameters used for characterisation of the CO_2 system in organic-rich waters. However, for biogeochemical modellers the implications are less clear. The only two CO_2 parameters that behave conservatively on mixing are *DIC* and *TA*, which raises two questions: first, is titration alkalinity that includes an organic contribution conservative on mixing?; and second, how can the titration alkalinity be used in estimating other CO_2 system parameters in a biogeochemical model?

In order to test whether the titration alkalinity is conservative, calculations were carried out using the GIVAKT model. Low salinity, organic-rich Baltic seawater (S=3, [FA]=10 mg L^{-1}, *TA*=800 µmol kg^{-1}, *DIC*=790 µmol kg^{-1}) was diluted with organic-free seawater (S=35, *TA*=2200 µmol kg^{-1}, DIC=2000 µmol kg^{-1}) at 25°C (Figure 8). A control run was made by diluting organic-free Baltic seawater of the same composition with organic-free seawater. The resulting mixtures were then used to generate modelled titrations that were analysed using the different evaluation procedures. The differences between modelled *TA* and *TA* expected from conservative mixing lines are shown in Figure 9.

For the dilution of organic-free Baltic seawater, the modified Gran function based on concentration output from the model, exactly reproduces the target concentrations of the mixing line. Results from the script-based evaluation methods vary slightly, but are within the general precision of the methods. For the dilution of organic-rich Baltic seawater, the modified Gran function varied significantly (< 4 µmol kg^{-1}) along the salinity gradient. Results from the script-based evaluation methods varied non-linearly along the gradient and significant differences of up to 12 µmol kg^{-1} at low salinities and high FA concentrations were observed. As the sample gets more diluted, the discrepancies are reduced. The resulting effect of this dilution experiment on the organic alkalinity is shown in Figure 8. The difference in Figure 9 between the Gran evaluation based on bicarbonate concentrations from GIVAKT, and the Gran evaluations based on fitted bicarbonate concentrations suggests strongly that it is the continued protonation of the organic matter following the endpoint that leads to poor estimates of the bicarbonate concentrations and thus erroneous estimates of the total alkalinity.

4.5 Estimating the organic alkalinity from DOC concentration

Kulinski et al. (2014) defined a bulk dissociation constant K_{DOM} to describe the relationship between the estimated organic alkalinity A_{org} and the DOC concentration:

$$K_{\mathrm{DOM}} = \frac{[\mathrm{H}^{+}]_{T} A_{org}}{f\,[\mathrm{DOC}] - A_{org}} \tag{6}$$

where $[\mathrm{H}^+]_\mathrm{T} = 10^{-\mathrm{pH}_\mathrm{T}(25°)}$, i.e., $[\mathrm{H}^+]_\mathrm{T} = [\mathrm{H}^+] + [\mathrm{HSO_4^-}]$ at 25°C, and f is the fraction of DOC considered to contribute to A_{org}. The values of pK_{DOM} and f are obtained by non-linear fitting, and the revised data shown in Table 1 give values of 7.34 and 0.12 for pK_{DOM} and f, respectively (Table 4) (cf. 7.53 and 0.14 given in Kuliński et al. (2014)). This approach is equivalent to adding a term A_{org} to Equation (1).

The standard deviation of the differences is 2.3 µmol kg^{-1}, which is considerably less that the deviations observed in Figure 9, albeit over a limited salinity range. In addition, the fitted value of f agrees well with the assumption that the DOC consists of WHAM fulvic acid.

WHAM FA has a total of 7.8 mmol g^{-1} ionisable sites. Assuming the fulvic acid to be 50% carbon, this gives 0.173 mol per mol C, of which the two shaded areas in Figure 6 correspond to 0.125 mol per mol C, very close to the fitted value of f, 0.12. Given the assumptions involved, this is excellent agreement. Since this representation of A_{org} is necessarily conservative to mixing, this simple approach may provide the best available method of representing organic alkalinity in biogeochemical models at the current state of knowledge.

5. Summary and conclusions

Organic matter in freshwater systems is known to comprise a polydisperse mixture that ionises over a wide pH range. The presence of such polydisperse organic matter in marine waters invalidates the assumptions on which the current definition of titration alkalinity is based. The modelling work presented here shows that the organic alkalinity estimated from measurements in the Baltic Sea (23 – 34 mol kg^{-1}) is consistent with the dissolved organic carbon present consisting of terrestrial humic substances as represented by the WHAM model. However, continued protonation of the organic matter beyond the normal titration endpoint at pH ≈ 4.5 introduces uncertainties into the titration evaluation codes, which assume that only inorganic acid-base systems are present. A direct test of the relevance of the WHAM model for organic alkalinity could be carried out by following an alkalinity titration with a back-titration in an inert atmosphere after removing all CO_2 from the system. The major contributors to this titration would be the protonation of fluoride, organic matter and borate, with the organic matter probably dominating up to neutral pH. The resulting back titration could then be analysed to assess the extent of agreement with the WHAM model.

Further work is needed, over a wider salinity range and in different estuarine and brackish waters, in order to examine the wider significance of this approach. In particular, whether organic alkalinity can be directly calculated from the DOC concentration in organic-rich brackish waters other than the Baltic Sea.

Analysis and modelling of the CO_2 system in organic-rich waters should take account of the existence of organic alkalinity. For experimental measurements, this involves measuring at least two other CO_2 parameters so that the inorganic alkalinity can be calculated. For biogeochemical modelling, this involves treating the total alkalinity as a quantity that is conservative with mixing, and subtracting the organic alkalinity estimated from DOC in order to obtain the inorganic alkalinity for further calculations on the CO_2 system. The organic alkalinity derived from DOC in Equation (6),which is used to add a term A_{org} to Dickson's definition, is implicitly assumed to be independent of changes in salinity, temperature, and pressure. Since the data required to characterise these dependencies is lacking, equation (6) constitutes the best method currently available for assessing the organic contribution to alkalinity. It should be noted that, although the organic alkalinity – DOC relationship is currently based on very few data in a single brackish water body, the Baltic Sea, these results may also contribute to understanding the "excess alkalinity" of the order of 4 µmol kg^{-1} recently observed in an overdetermination of the CO_2 system in seawater (Patsavas et al., 2014).

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Figures and figure captions

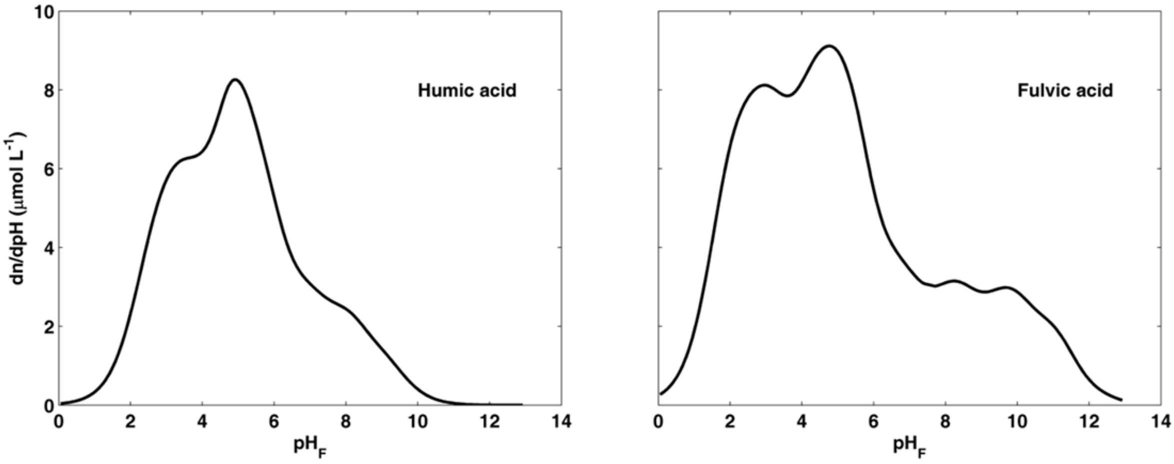

Figure 1. Typical dn/dpH as a function of pH for 7 mg L^{-1} WHAM material in Baltic seawater (S=6.15, T=25°, DIC=1470 μmol L^{-1}); humic acid (left) and fulvic acid (right).

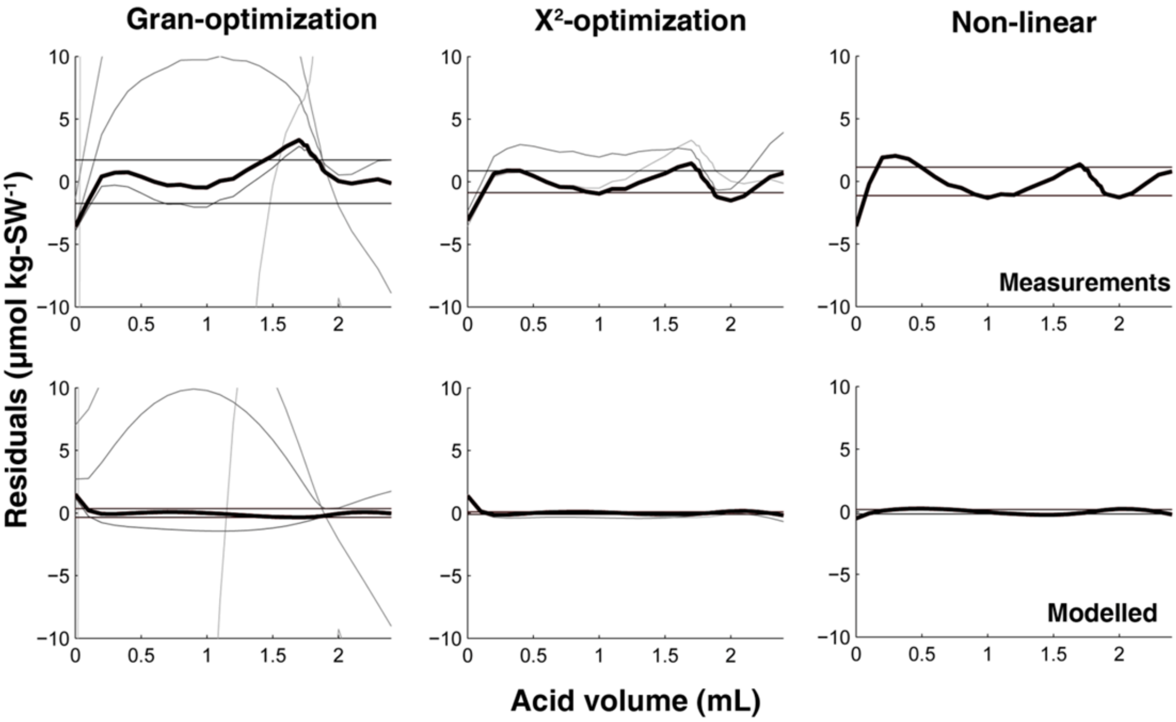

Figure 2. Residuals in *TA* (µmol kg^{-1}) for different evaluation methods of the test data (upper panel) as given by Dickson et al. (2007) and, corresponding model data provided by GIVAKT (lower panel). Grey lines indicate earlier iteration steps and the lower and upper limits of the root mean square are given by the horizontal lines. The equivalence volume is approximately 1.9 mL.

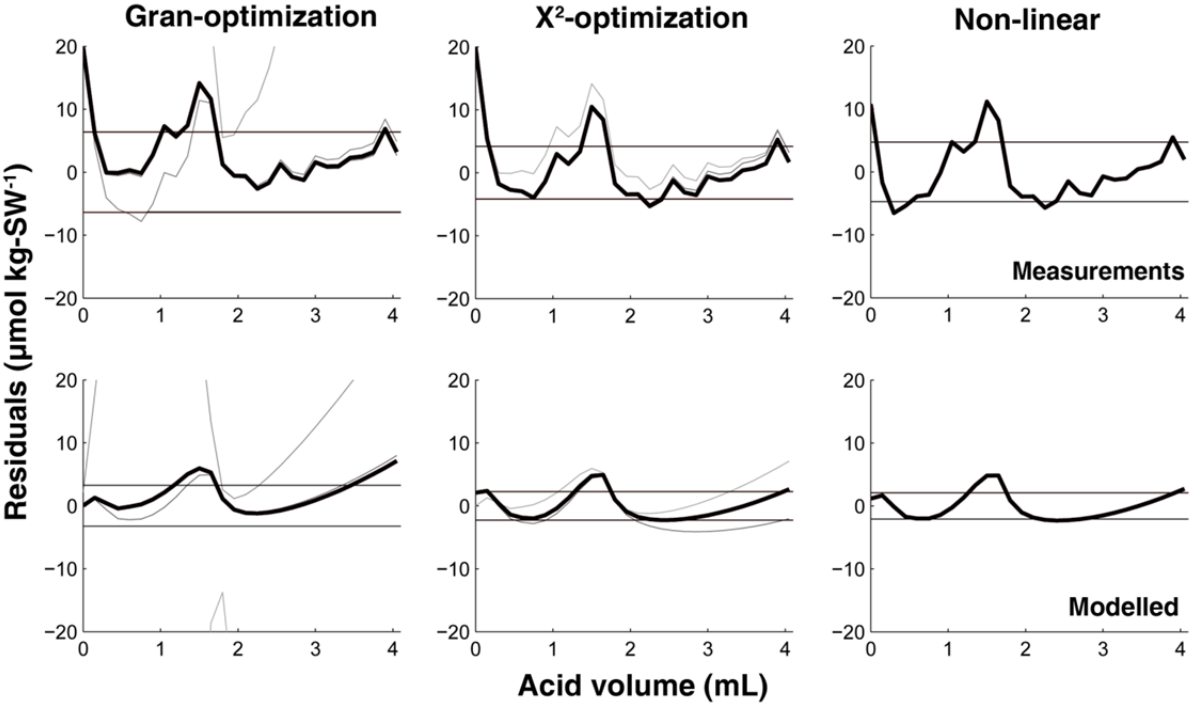

Figure 3. Residuals in *TA* (µmol kg^{-1}) for different evaluation methods of organic-rich Baltic water titration data (Station 3, Table 1; upper panel) and corresponding theoretical titration data provided by the humic seawater model (lower panel). Grey lines indicate earlier iteration steps and the lower and upper limits of the root mean square are given by the horizontal lines. The equivalence volume is approximately 1.7 mL.

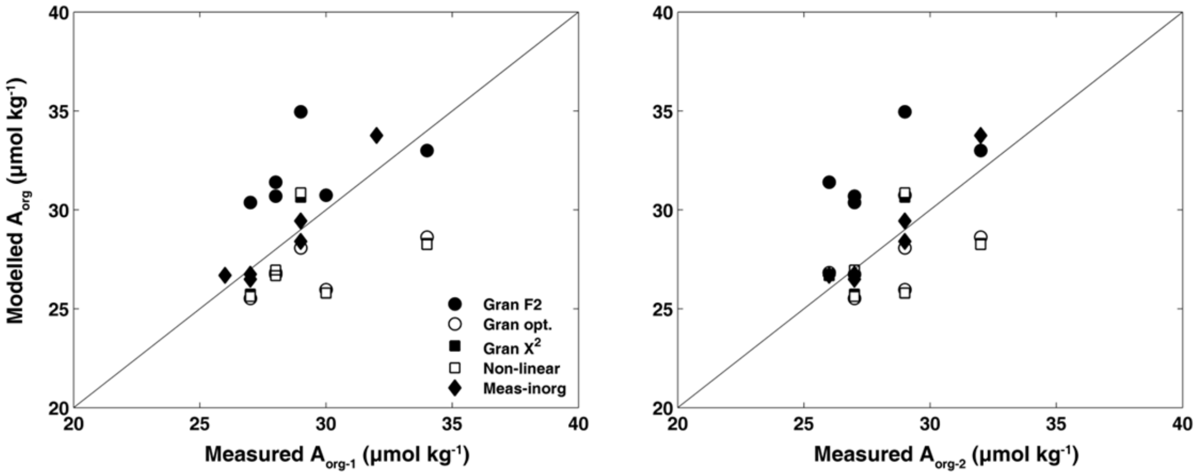

Figure 4. Modelled organic alkalinity (A_{org}), evaluated by different methods, compared to measured organic alkalinity according to Kuliński et al. (2014). A_{org-1} was determined as the difference between the measured total alkalinity and that calculated from *DIC* and pH_T. A_{org-2} is the difference between measured *TA* and *TA* calculated from *DIC* and pCO_2. Filled circles denote the difference between the measured *TA* and the inorganic alkalinity as given by GIVAKT.

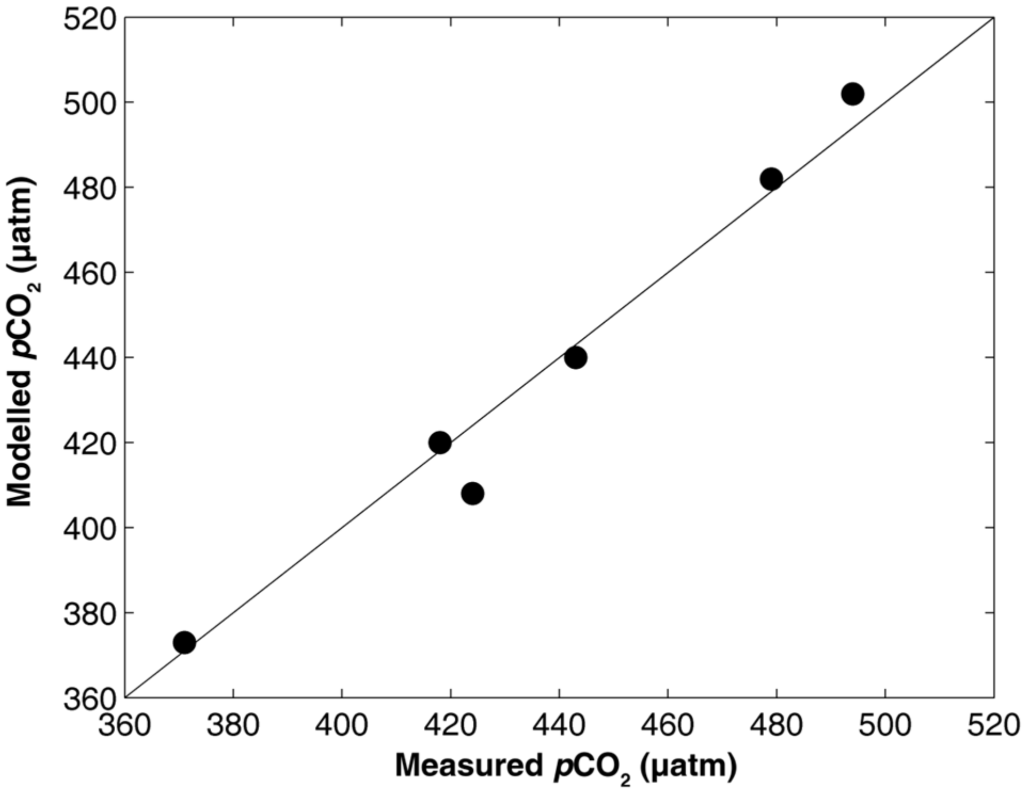

Figure 5. Modelled pCO$_2$, evaluated by different evaluation methods, compared to measured pCO$_2$ at in situ temperature according to Kuliński et al. (2014).

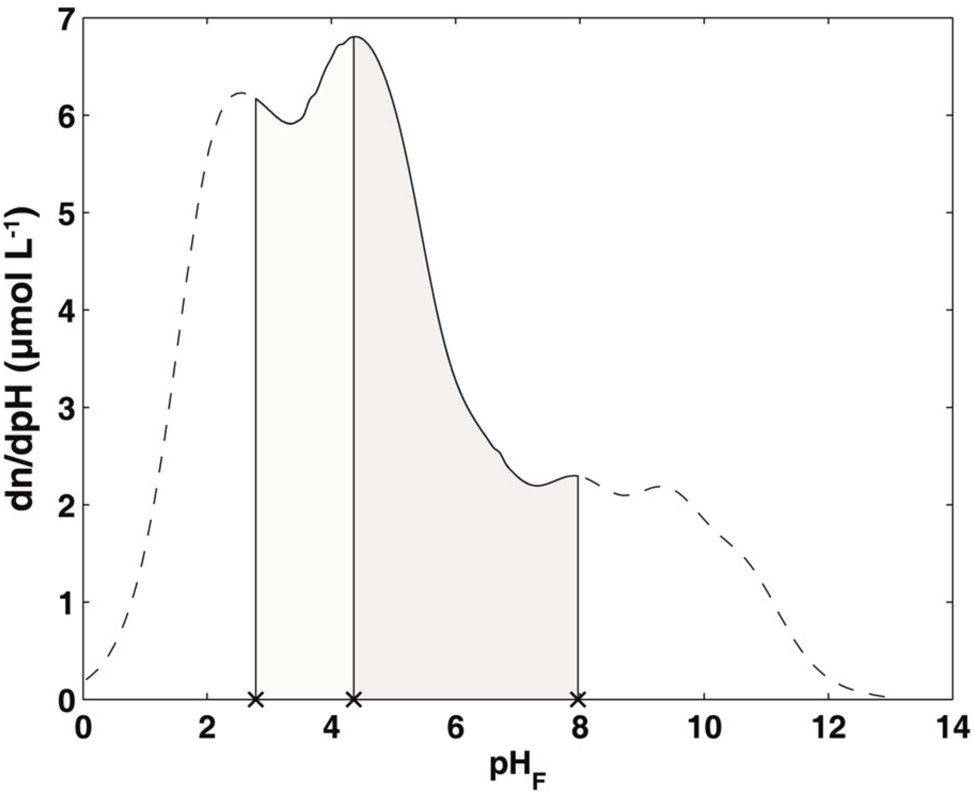

Figure 6. Plot of the difference derivative of the charge as a function of pH. The darker shaded area indicates the sum of the charged sites of FA that have been protonated during the titration between the initial sample pH and the pH at the equivalence point, i.e., the organic alkalinity. The lighter shaded area indicates the additional needed excess organic alkalinity in order to match the *TA* determined from conventional evaluation methods.

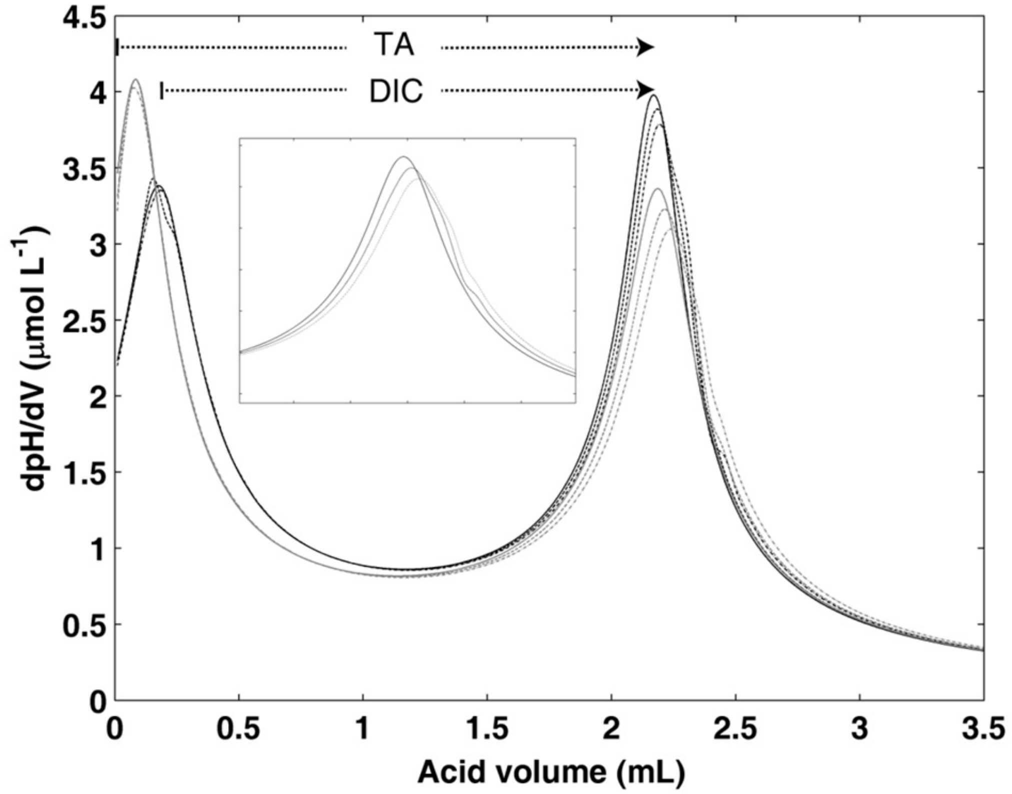

Figure 7. Plot of the difference derivative of pH against acid volume for modelled titrations of (i) seawater of salinity 35 with 0, 5, and 10 mg FA L^{-1} (black lines) and (ii) Baltic seawater of salinity 10 with 0, 5, 10 mg FA L^{-1} (grey lines). Inset shows a close-up of the peaks of the second equivalence points for the Baltic seawater.

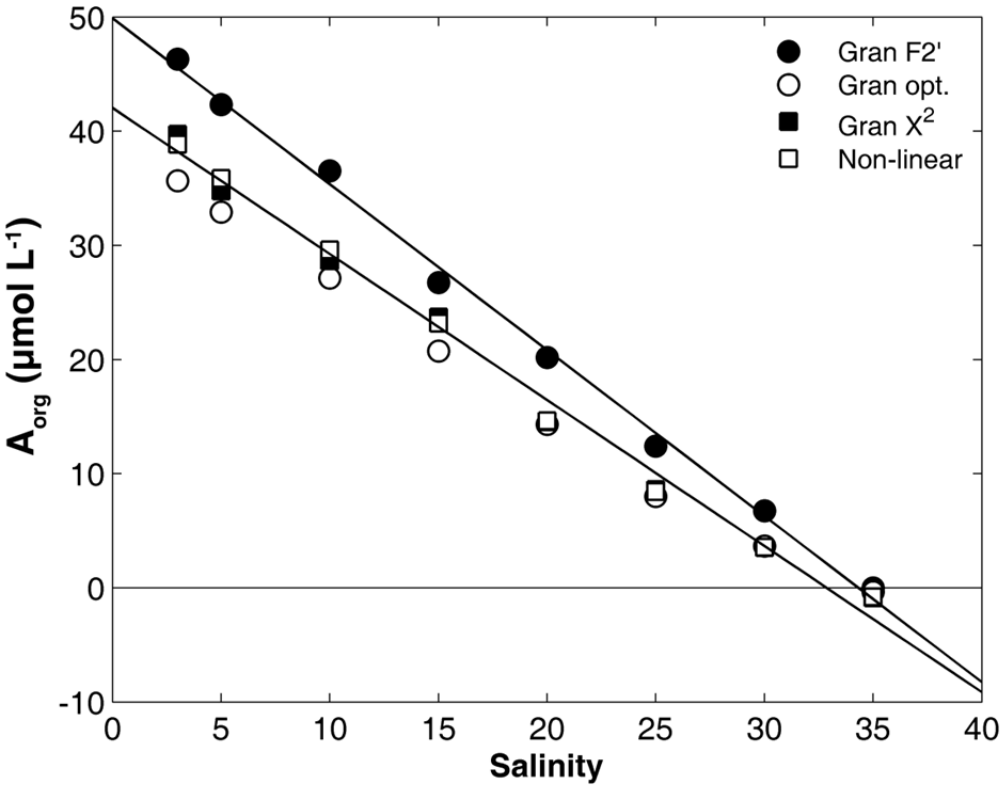

Figure 8. Organic alkalinity as a function of salinity when diluting typical low salinity, organic-rich Baltic seawater with organic-free seawater at 25°C. The black lines indicate linear fits of the results given by the modified Gran function (F2´) and the non-linear curve fitting procedure.

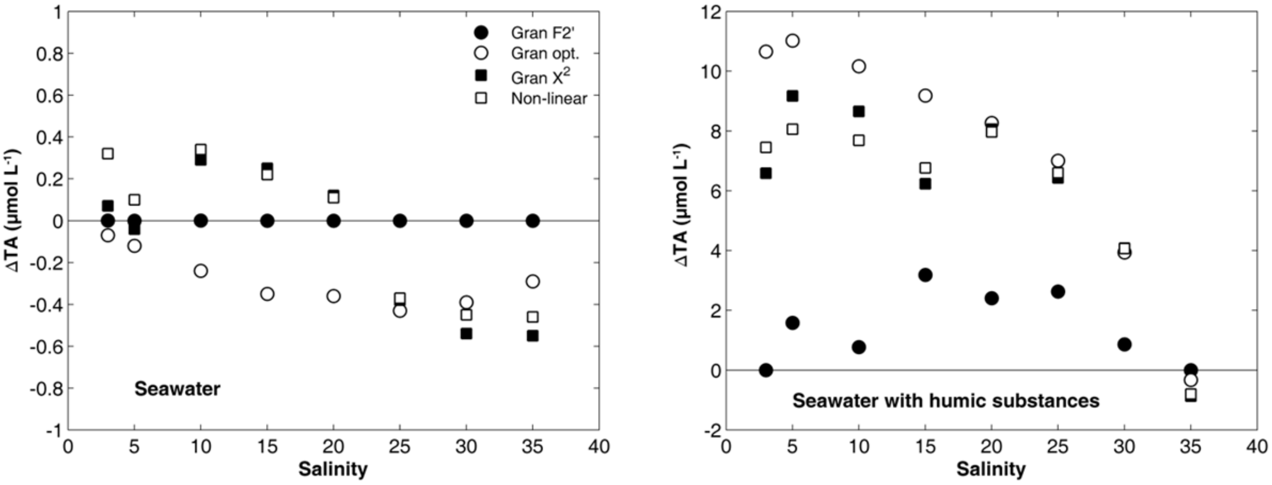

Figure 9. Differences between modelled *TA* and *TA* according to mixing line from dilution of organic-free (left) and organic-rich (right) Baltic seawater with organic-free seawater as a function of salinity for different evaluation methods.

Tables and table captions

Table 1. Results from Kulinski et al. (2014) from the Baltic Sea in 2011 used in this study, A_{org-1} was calculated as the difference between the titration alkalinity and that calculated from *DIC* and pH_T. A_{org-2} is the difference between measured *TA* and *TA* calculated from *DIC* and pCO_2. The values in parentheses are the contribution of A_{org} to measured *TA*. All concentrations are in μmol kg^{-1}, except for DOC (μmol L^{-1}) and pCO_2 (μatm).

Station no.	Salinity	t °C	[DOC]	*DIC*	pH_T (25°C)	*TA*	pCO_2	A_{org-1}	A_{org-2}
1	8.165	8.2	319	1650	7.735	1694	494	30 (1.8%)	29 (1.7%)
3	7.652	8.5	313	1659	7.800	1709	443	27 (1.6%)	27 (1.6%)
5	7.198	9.4	318	1589	7.869	1648	371	28 (1.7%)	26 (1.6%)
8	6.772	8.4	340	1572	7.801	1624	424	34 (2.1%)	32 (2.0%)
13	6.155	8.1	316	1469	7.787	1508	418	28 (1.8%)	27 (1.8%)
18	2.843	6.1	344	794	7.532	800	479	24 (2.9%)	23 (2.8%)

Table 2. Fitted parameters (*TA*, *DIC*, $E°$, pK_1*) from the evaluation of practical and theoretical titration curves by different evaluation methods in Figure 2. The results are reported as the difference of the estimated values and the target values as given by Dickson et al. (2007). The number of iterations is shown in the last column.

	TA μmol kg^{-1}	***DIC*** μmol kg^{-1}	***E°*** mV	**pK_1***	**Std.** μmol kg^{-1}	**Its.**
Target values (test data)	2320.21	2344.26	393.609	5.909	1.209	9
Target values (model data)	2320.21	2344.26	400	5.862		
Test data	**Δ*TA***	**Δ*DIC***	**Δ*E°***	**ΔpK_1**	***TA* rms**	**Its.**
Gran-optimization	2.11	5.86	0.118	0.003	1.74	7
χ^2-optimization	-0.42	3.2	-0.027	0.001	0.87	2
Non-linear	0	0	0	0	1.13	9
Model data						
Gran-optimization	-0.33	1.45	6.072	0.015	0.36	7
χ^2-optimization	0.02	1.86	6.052	0.015	0.10	2
Non-linear	0.15	0.21	6.046	0.015	0.18	9

Table 3. Fitted parameters (*TA*, *DIC*, *E*°, pK_1) from the evaluation of practical and theoretical titration curves of organic-rich Baltic seawater (Station 3, Table 1) by different evaluation methods. The number of iterations is shown in the last column.

	TA µmol kg^{-1}	***DIC*** µmol kg^{-1}	***E*°** mV	**pK_1**	***TA* rms** (MSE)	**Its.**
Target values (field data)	1709	1659	590.722	6.084	0.069	-
Target values (model data)	1709	1659	600	6.034		
Field data	**Δ*TA***	**Δ*DIC***	**Δ*E*°**	**ΔpK_1**	***TA* rms**	**Its.**
Gran-optimization	-4	-	2.679	0.026	6.372	6
X^2-optimization	-1	-	2.695	0.029	4.182	2
Non-linear (potential)	0	-	2.705	0.023	4.719	8
Model data						
Gran-optimization	1	-20	-5.504	-0.019	3.241	5
X^2-optimization	1	-18	-5.556	-0.022	2.275	2
Non-linear (potential)	1	-19	-5.553	-0.021	2.083	8

Table 4. Comparison between measured organic alkalinity (Table1), and organic alkalinity calculated using Equation (6).

			Measured		Calculated		Difference	
Station no.	**DOC**	**pH$_{tot}$ (25°C)**	**A$_{org-1}$**	**A$_{org-2}$**	**A$_{org-1}$**	**A$_{org-2}$**	**A$_{org-1}$**	**A$_{org-2}$**
1	319	7.735	30.4	29.4	27.3	27.3	2.7	1.7
3	313	7.800	26.8	27.0	27.9	27.9	-0.9	-0.9
5	318	7.869	27.7	25.7	29.5	29.5	-1.5	-3.5
8	340	7.801	34.1	32.1	30.3	30.3	3.7	1.7
13	316	7.787	27.9	27.4	28.0	28.0	0.0	-1.0
18	344	7.532	23.9	23.0	25.2	25.2	-1.2	-2.2