



## Acid-base properties of Baltic Sea dissolved organic matter



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### ABSTRACT

Calculations related to the marine CO<sub>2</sub> system that are based on alkalinity data may be strongly biased if the contributions of organic compounds are ignored. In coastal seas, concentrations of dissolved organic matter (DOM) are frequently high and alkalinity from inorganic compounds is low. In this study, based on measurements of total alkalinity, total CO<sub>2</sub>, and pH, we determined the organic alkalinity,  $A_{org}$ , in water from the central Baltic Sea. The maximum  $A_{org}$  measured in the surface mixed layer during the spring bloom was > 50 μmol/kg-SW but the  $A_{org}$  decreased with depth and approached zero below the permanent halocline. This behavior could be attributed to the decreased pH of deeper water layers. The data were used to calculate the bulk dissociation constant,  $K_{DOM}$ , for marine DOM and the fraction  $f$  of dissolved organic carbon (DOC) that acts as a carrier for acid-base functional groups. The  $pK_{DOM}$  (7.27) agreed well with the value (7.34) previously estimated in a preliminary study of organic alkalinity in the Baltic Sea. The fraction of carbon atoms carrying acid-base groups was 17% and was somewhat higher than previously reported (12%). Spike experiments performed using artificial seawater and three different humic/fulvic substances tested whether the acid-base properties of these substances explain the results of our field study. Specifically,  $A_{org}$  was determined at different concentrations (DOC) of the added humic/fulvic substances. The relationship between  $A_{org}$  and the DOC concentrations indicated that humic/fulvic substances are more acidic ( $pK_{DOM} < 6.5$ ) than the bulk DOC natural occurring in the Baltic Sea.

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### 1. Introduction

The marine CO<sub>2</sub> system is currently the focus of many investigations in marine research aimed at understanding the oceanic uptake of anthropogenic CO<sub>2</sub>, ocean acidification phenomena and biogeochemical processes linked to the consumption or production of CO<sub>2</sub>. Four measurable key variables are currently used to characterize the marine CO<sub>2</sub> system: Total CO<sub>2</sub> ( $C_T$ ), total alkalinity ( $A_T$ ), pH and the CO<sub>2</sub> partial pressure ( $pCO_2$ ). In general, any two of these variables are sufficient to determine the other two as well as several properties of the CO<sub>2</sub> system, on the basis of the carbonic acid dissociation constants. However, strictly speaking, this is not the case if  $A_T$  is used in the calculations because it is defined as an excess of proton acceptors ( $pK \geq 4.5$ ) over proton donors ( $pK < 4.5$ ) (Dickson, 1981) and thus refers to the status of all acid-base components in seawater. This is not problematic for ocean water in which borate (except for

phosphate and silicate in the deep or stagnant waters) is the only relevant  $A_T$  contribution adding to the carbonate alkalinity, as it can easily be determined from the constant boron/salinity ratio in ocean water.

By contrast, in estuarine and coastal waters, where high concentrations of dissolved organic matter (DOM) may affect the acid-base system, an assessment of the marine CO<sub>2</sub> system is less straightforward. Surface concentrations of dissolved organic carbon (DOC, representing DOM) in the ocean are in the range 60–90 μmol C/L (Hansell and Carlson, 2014) whereas in coastal waters such as the Baltic Sea the DOC load is considerably higher, with concentrations with a mean between 300 and 330 μmol C/L for the Baltic Proper (Feistel et al., 2008). Additionally,  $A_T$  in some regions of the Baltic Sea may be as low as a few 100 μmol/kg-SW in contrast to the >2000 μmol/kg-SW of ocean waters. Hence, the share of organic compounds in  $A_T$  in Baltic Sea surface water may be large.

Several studies have described the substantial impact of DOM on  $A_T$  (Cai et al., 1998; Hernández-Ayón et al., 2007; Hernández-Ayón et al., 1999; Hongve, 1990; Hruška et al., 2003; Kim and Lee, 2009; Yang et al., 2015). Kuliński et al. (2014) determined the  $C_T$ ,  $A_T$ , pH and  $pCO_2$  of seawater samples spiked with DOC extracts from river water and found large differences between the measured  $pCO_2$  and

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the  $p\text{CO}_2$  calculated from  $C_T$  and  $A_T$  assuming only the presence of inorganic  $A_T$  (carbonates and borate). The 26–56% lower  $p\text{CO}_2$  correlated with the added DOM, which obviously affected the alkalinity. Therefore, the values determined for the  $\text{CO}_2$  system in waters with high DOM loads may be questionable if the calculations include measurements of  $A_T$  limited to inorganic components. This consideration is also relevant to biogeochemical models that use the conservative variables of  $A_T$  and  $C_T$  to simulate the marine  $\text{CO}_2$  system. However, current knowledge regarding the complex composition and structure of DOM does not yet allow the inclusion of the acid-base properties of individual organic acids into numerical models.

Instead, in the more practical approach suggested by Hernández-Ayón et al. (1999), Kim and Lee (2009), Köhler et al. (2000), Kuliński et al. (2014) and Muller and Bleie (2008) the effect of organic compounds on  $A_T$  was characterized using the term  $A_{\text{org}}$  defined as the difference between the measured  $A_T$  and the  $A_T$  calculated from measurements of  $C_T$  and pH. The latter ignores organic contribution and thus corresponds to the inorganic alkalinity:

$$A_{\text{org}} = A_{T(\text{measured})} - A_{T(\text{calculated})} \quad (1)$$

Kuliński et al. (2014) defined a bulk dissociation constant,  $K_{\text{DOM}}$ , for the fraction  $f$  of DOC that acts as a carrier of acid-base groups and therefore has the potential to generate  $A_{\text{org}}$ . The corresponding apparent dissociation equilibrium may then be expressed as:

$$K_{\text{DOM}} = \frac{[\text{H}^+][A_{\text{org}}]}{f c_{\text{DOC}} - A_{\text{org}}} \quad (2)$$

Based on measurements of the  $A_T$ ,  $C_T$  and pH of Baltic Sea surface water, Kuliński et al. (2014) determined  $A_{\text{org}}$  according to Eq. (1) and used Eq. (2) to determine  $f$  and  $K_{\text{DOM}}$  applying a nonlinear least square Gauss-Newton fit. However, the study was based on a rather limited set of samples ( $n = 6$ ) and must be considered as a first attempt to quantitatively account for the effect of organic compounds on the acid-base system of the Baltic Sea. The primary aim of

the present study was to examine the acid-base properties of DOM in the Baltic Sea that were reported in the study of Kuliński et al. (2014). To do so, the number of analyzed samples was increased considerably and, more importantly, because sampling was performed at different depths and seasons, the samples cover a much broader pH range. Thus, the uncertainties in the calculations of  $f$  and  $K_{\text{DOM}}$  could be reduced substantially.

In lab experiments carried out in parallel, the  $A_T$ ,  $C_T$  and pH of artificial seawater spiked with pure humic substances were determined. This allowed us to test whether the acid-base properties of humic substances explain the  $K_{\text{DOM}}$  obtained from the field study.

## 2. Materials and methods

### 2.1. Field study

In 2014 and 2015, seven vertical profiles were collected, in February, March, May, and November. Samples for the determination of  $A_T$ ,  $C_T$ , and pH were taken at station BY15 located in the Gotland Basin in the central Baltic Sea (Fig. 1) and sampled from a CTD rosette avoiding any gas exchange with ambient air and were collected in 250 mL Schott® Duran bottles that were closed by a stopper and fixed with a clamp, but without additional grease sealing. Each sample was poisoned with 500  $\mu\text{L}$  of saturated mercury chloride solution and then stored at 5 °C in the dark until analyzed onshore. The pH across the total scale was measured spectrophotometrically using a semi-automated measurement system designed by Carter et al. (2013). The influence of the indicator m-cresol purple (TCI Europe, unpurified) on the pH of the seawater samples was corrected using a modified MATLAB version of CO2sys (Pelletier et al., 2007) as recommended by Hammer et al. (2014). The accuracy of the spectrophotometric measurements was validated by measurements of TRIS (Tris(hydroxymethyl)aminomethane)-buffer-solutions and Carbon Reference Material, (CRM, Dr. A. Dickson, University of California, San Diego) certified for  $C_T$  and  $A_T$  concentrations. The deviations ranged from  $\pm 0.01$  to  $\pm 0.02$  and the precision was  $\pm 0.00065$

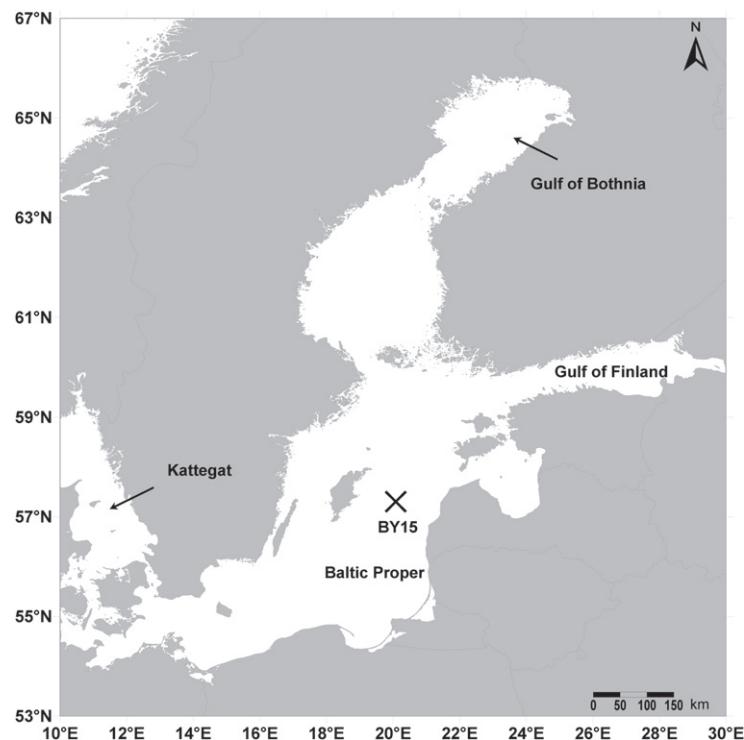


Fig. 1. Map of the Baltic Sea, Sampling station BY15, located at the Gotland Deep, is indicated (X).

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