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Contribution of non-carbonate inorganic and organic alkalinity to total measured alkalinity in pore waters in marine sediments (Gulf of Gdansk, S-E Baltic Sea)

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ABSTRACT

Various microbiological, chemical and physical processes during early diagenesis in marine sediments make the chemical composition of pore water significantly different from that of the sea water. The aim of this study was (a) to compare concentrations of total alkalinity measured using titration method ($TA_{meas.}$) with carbonate alkalinity calculated ($TA_{calc.}$) from dissolved inorganic carbon and pH, and (b) to determine the proportion of non-carbonate inorganic bases (N-CIBs) and alkalinity from organic compounds (OA) in $TA_{meas.}$ in pore water in the Gulf of Gdansk. In the study, $TA_{meas.}$ as well as concentrations of dissolved inorganic and organic carbon (DIC and DOC), hydrogen sulphide, sulphate, ammonium, phosphates and borate in near-bottom and pore water were measured at three sampling sites in October 2013. At all the sites, $TA_{meas.}$ was 1632–14,460 μmol kg^{-1} and increased with depth into the sediment, as did the concentrations of other parameters (excluding sulphate). Inorganic and organic compounds produced during organic matter (OM) decomposition in sediments had a considerable contribution to $TA_{meas.}$ in pore water. As a result $TA_{meas.}$ was up to 38% higher than $TA_{calc.}$ The observed excess alkalinity (TA_{excess}) was from 56 to 3972 μmol kg^{-1} and increased gradually going deeper into the sediment. TA_{excess} was correlated with concentration of N-CIBs (mainly hydrogen sulphide, ammonia and phosphates) and DOC present in pore water. The main source of N-CIBs in pore water was bacterial sulphate reduction during OM mineralization. The concentration of N-CIBs in pore water ranged from 85 to 1053 μmol l^{-1} and the percentage share of N-CIBs in $TA_{meas.}$ was 4–35%. The highest proportion of N-CIBs in $TA_{meas.}$ was observed in the upper (0–12 cm) layers of the sediment. Anoxic decomposition of OM has led to the production of OA in pore water which constituted up to 26% of $TA_{meas.}$ The concentration of OA varied from 2 to 2953 μmol $l^{-1}$and at all sites increased with depth into the sediment. This is due to the accumulation of products of decomposition of OM in pore water, i.e. organic acids and fulvic and humic acids.

1. Introduction

Total alkalinity (TA) is one of the most frequently studied parameters in the marine environment. It has been used for many years to determine the neutralising capacity of sea water (e.g. Pytkowicz and Atlas, 1975). TA, along with other parameters, such as pH or dissolved inorganic carbon, is used for the estimation of the partial pressure of carbon dioxide (pCO_2) (e.g. Wanninkhof et al., 1999; Lueker et al., 2000). TA can be defined as the number of hydrogen ions (in millimoles) needed to neutralise weak bases in 1 kg of sea water (Grasshoff et al., 1999). Dickson's (1981) definition is more accurate, describing TA as the number of H^+ moles equivalent to the excess of proton acceptors (i.e. bases formed from weak acids with a dissociation constant $K \leq 10^{-4.5}$, at 25 °C) over proton donors (acids of $K > 10^{-4.5}$) in 1 kg of a sample.

The higher the alkalinity of sea water, the greater its capacity to resist pH changes. In the surface water of the World Ocean, alkalinity is correlated with salinity and sea surface temperature (Millero et al., 1998; Lee et al., 2006). Regional differences result from the same factors that shape salinity. Aside from that, alkalinity is influenced by biological, chemical and physical processes occurring with various intensity, such as precipitation and dissolution of biogenic $CaCO_3$ as well as the upwelling of deepwater of higher alkalinity (Millero et al., 1998).

In open ocean waters, where the concentration of other bases is inconsiderable in comparison to dissolved inorganic carbon, TA is determined mainly by bicarbonate, carbonate and borate ions:

$$TA = [HCO_3^{-}] + 2\left[CO_3^{2-}\right] + [B(OH)_4^{-}] + [OH^{-}] - [H^{+}] \quad (1)$$

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This is why TA, along with other parameters, can be used for the calculation of concentration of species of the carbonate system in seawater (Lueker et al., 2000; Wolf-Gladrow et al., 2007).

However, in anoxic conditions, ammonium or hydrogen sulphide can have a considerable contribution to TA (Dickson, 1981; Hiscock and Millero, 2006):

$$\begin{aligned}\mathrm{TA} = {} & [\mathrm{HCO_3}^-] + 2\left[\mathrm{CO_3}^{2-}\right] + \left[\mathrm{B(OH)_4}^-\right] + [\mathrm{OH}^-] + \left[\mathrm{HPO_4}^{2-}\right] \\ & + 2\left[\mathrm{PO_4}^{3-}\right] + \left[\mathrm{SiO(OH)_3}^-\right] + [\mathrm{NH_3}] \\ & + [\mathrm{HS}^-] - [\mathrm{H}^+] - [\mathrm{HSO_4}^-] - [\mathrm{HF}] - [\mathrm{H_3PO_4}] \qquad (2)\end{aligned}$$

In estuaries, on the other hand, an additional source of alkalinity can be carboxylic acid groups or phenolic groups found in dissolved organic matter (DOM) (Cai et al., 1998; Hernández-Ayon et al., 2007; Muller and Bleie, 2008; Kuliński et al., 2014).

An exceptional environment, where the difference between carbonate alkalinity (originating from $[\mathrm{HCO_3^-}]$ and $[\mathrm{CO_3^{2-}}]$) and total alkalinity is particularly noticeable, is pore water of marine sediments. As a result of a series of microbiological and abiotic reactions (dissolution/precipitation) during early diagenesis, the chemical composition of pore water is significantly different from that of the sea water (e.g. Carman and Rahm, 1997; Chatterjee et al., 2011). Earlier studies showed that the alkalinity in pore water can be a few or even 20 times higher than in sea water (Berner et al., 1970; Carman and Rahm, 1997; Chatterjee et al., 2011; Lukawska-Matuszewska and Kielczewska, 2016). The processes of exchange of substances across sediment-water interface (benthic exchange) make pore water a significant source of alkalinity for the water column (Carman and Rahm, 1997; Cyronak et al., 2013; Cyronak and Eyre, 2016; Drupp et al., 2016).

The main process that generates alkalinity in a fine-grained organic rich sediments is anoxic mineralisation of organic matter (OM), mainly through denitrification and sulphate reduction, and by the reduction of Mn IV and Fe III (Berner et al., 1970):

$$\begin{aligned}&(\mathrm{CH_2O})_{106}(\mathrm{NH_3})_{16}(\mathrm{H_3PO_4}) + 84.8\ \mathrm{HNO_3} \rightarrow 106\ \mathrm{CO_2} + 42.2\ \mathrm{N_2} \\ &\quad + 148\ \mathrm{H_2O} + 16\ \mathrm{NH_3} + \mathrm{H_3PO_4} \qquad (3)\end{aligned}$$

$$\begin{aligned}&(\mathrm{CH_2O})_{106}(\mathrm{NH_3})_{16}(\mathrm{H_3PO_4}) + 53\ \mathrm{SO_4}^{2-} \rightarrow 106\ \mathrm{HCO_3}^- + 53\ \mathrm{H_2S} \\ &\quad + 16\mathrm{NH_3} + \mathrm{H_3PO_4} \qquad (4)\end{aligned}$$

$$\begin{aligned}&(\mathrm{CH_2O})_{106}(\mathrm{NH_3})_{16}(\mathrm{H_3PO_4}) + 236\ \mathrm{MnO_2} \rightarrow 236\ \mathrm{Mn}^{2+} + 106\ \mathrm{CO_2} \\ &\quad + 8\ \mathrm{N_2} + 366\ \mathrm{H_2O} + \mathrm{H_3PO_4} \qquad (5)\end{aligned}$$

$$\begin{aligned}&(\mathrm{CH_2O})_{106}(\mathrm{NH_3})_{16}(\mathrm{H_3PO_4}) + 212\ \mathrm{Fe_2O_3} + 848\ \mathrm{H}^+ \rightarrow 424\ \mathrm{Fe}^{2+} \\ &\quad + 106\ \mathrm{CO_2} + 16\ \mathrm{NH_3} + 530\ \mathrm{H_2O} + \mathrm{H_3PO_4} \qquad (6)\end{aligned}$$

What inclined the author to conduct the research presented here were personal observations of the fact that in pore water in the Gulf of Gdansk total alkalinity measured using the titration method is often much higher than the concentration of dissolved inorganic carbon. At the same time, a significant correlation was observed between titration alkalinity and phosphates, ammonium, hydrogen sulphide and dissolved organic carbon. The aim of this paper is to determine the proportion of non-carbonate inorganic bases (N-CIBs) and organic alkalinity (OA) in total alkalinity measured using the titration method ($\mathrm{TA_{meas.}}$) in pore water in the Gulf of Gdansk. A secondary aim is to determine the correlation between $\mathrm{TA_{meas.}}$ and dissolved inorganic carbon (DIC) and organic carbon (DOC) and to discuss the processes that influence $\mathrm{TA_{meas.}}$ in pore water in the Gulf of Gdansk.

2. Materials and methods

2.1. Study area

The Gulf of Gdansk is in the southeastern part of the Baltic Sea (Fig. 1), and is characterised both by large inflow of river water (dominated by the Vistula) and by high primary production (ca. 160 g C $\mathrm{m^{-2}\ y^{-1}}$) (Kruk-Dowgiałło and Szaniawska, 2008). The surface water of the gulf is separated from the deep, more saline water by a halocline occurring at a depth of about 60–80 m (Andrulewicz and Witek, 2002). The renewal of deepwater is possible owing to the inflow of highly saline and oxygenated water from the North Sea during the so-called Major Baltic Inflows (MBIs) (Meier et al., 2006). As a large load of OM, which results from the eutrophication of the gulf, reaches the seabed, it leads to the consumption of oxygen in deepwater (Burska and Graca, 2011). As a consequence, oxygen shortages or complete lack of oxygen often occur in bottom water. At times of stagnation between inflows nutrients are observed to accumulate under the halocline. Their source is mineralisation of OM in the water column and their release from sediments as a result of change of redox conditions (Carman and Rahm, 1997; Graca et al., 2006).

The study material was collected from three sites located in the Gulf of Gdansk (Fig. 1; Table 1). The geochemical properties of sediments at the sampling sites have been described in detail in an earlier publication (Lukawska-Matuszewska and Kielczewska, 2016) and what follows here is only a short overview. At all of the sites there are fine-grained sediments - clayey silt at W6 and silty clay at G7 and GD (Lukawska-Matuszewska and Kielczewska, 2016). The water content of sediments in the upper layer (0–2 cm) is 88–91%. The highest organic carbon content (OC) in that layer is found at the G7 site (Table 1). OC contents at W6 and GD are similar and slightly lower than at G7. The ratio of OC to total nitrogen (TN) at all sites is greater than the average ratio for fresh matter of marine origin (OC:TN = 6.6) as given by Redfield et al. (1963). At the same time, OC:TN increases as the depth of the site increases (Table 1).

The sites differ considerably in terms of depth and, following that, in terms of dissolved oxygen concentration (DO) in water above the sediment. During the year, the conditions at G7 change from normoxic to hypoxic (DO ≤2 ml $\mathrm{l^{-1}}$) depending on the season. At GD, the oxygen resources in the near-bottom stratum are renewed mainly during MBIs, which occur infrequently and irregularly. As a result, episodes of oxygen depletion in the near-bottom water occur more often at GD and also last longer than at G7. As follows from the data available in the ICES base (spanning the years 1954–2014), about 70% of results of DO concentration in the Gdansk Deep area are ≤2 ml $\mathrm{l^{-1}}$ (ICES, 2016). However, at sites within the Gulf of Gdansk (similar to G7 in terms of depth), the concentration of DO ≤2 ml $\mathrm{l^{-1}}$ occurs in about 35% of cases (ICES, 2016). At the W6 station, hypoxia occurs periodically, as a result of an input of large amounts of OM to the bottom. However, the mixing of waters and oxygen transportation from surface strata prevents long-term oxygen depletion in the near-bottom water. At the time of material collection for the present study, the concentration of DO at W6 and G7 was ≤0.90 ml $\mathrm{l^{-1}}$. In the bottom water at GD hydrogen sulphide was present (Table 1). At all sites benthic macrofauna was absent during the sampling.

2.2. Sampling

The study material was collected during a voyage aboard Polish Navy survey vessel, the ORP Heweliusz, between 02 and 05.10.2013. At each of the stations the temperature (T), salinity (S) (CTD probe MCTD3, Falmouth Sci.) and DO concentration (potentiometric titration with automatic titrator SM-Titrino 702, Metrohm and combined Pt-ring electrode; analytical precision ≤1.6%) were measured. 28–35 cm long cores of sediment were collected using a Niemistö core probe, equipped with 50 cm plexi tubes with 7.5 cm internal diameter. Pore

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