



Remineralization of terrestrial dissolved organic carbon in the Baltic Sea



Karol Kuliński^{a,*}, Karoline Hammer^b, Bernd Schneider^b, Detlef Schulz-Bull^b

^a Institute of Oceanology, Polish Academy of Sciences, IO PAN, ul. Powstańców Warszawy 55, 81-712 Sopot, Poland

^b Leibniz Institute for Baltic Sea Research, IOW, Seestrasse 15 Warnemünde, D-18119 Rostock, Germany

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ABSTRACT

To assess the remineralization dynamics of terrestrial dissolved organic carbon (tDOC) in Baltic Sea water a set of incubation experiments was performed. Baltic Sea water was spiked with low molecular weight (LMW) and high molecular weight (HMW) tDOC extracted from water of the rivers Vistula and Oder. In parallel, incubation experiments were performed with seawater in order to determine the remineralization dynamics of Baltic Sea DOC (mDOC) that is characteristic for the marine environment but not necessarily of marine origin. At 10 consecutive time steps in the course of an incubation period of 188 days, the concentrations of O₂ and total CO₂ (C_T) were measured to assess the O₂ consumption and CO₂ production. The latter was used as a measure for the DOC mineralization. Three DOC fractions having different reactivity were identified. The refractory fraction was predominant in all samples and amounted to 66% in mDOC and about 80% in the tDOC. Two fractions of bioavailable DOC, which differed significantly concerning their reactivity, were identified in both the mDOC and tDOC. The more reactive labile fraction contributed to about 3% to LMW and HMW tDOC whereas 10% of the mDOC consisted of labile DOC. The half-life time for labile DOC ranged between 3.2 d and 6.4 d. The less reactive bioavailable fraction, the semi-labile DOC, showed half-life times of weeks to months. The total bioavailable fraction of the mDOC (34%) was higher than that of tDOC by a factor of about 2. Furthermore, it was characterized by a bulk half-life time of 10.6 d that was significantly lower than those for tDOC from the two rivers (32.5 d and 21.7 d). The measurements of the oxygen consumption and total CO₂ production during the remineralization yielded a ΔO₂:ΔC_T molar ratio close to 1.0 for the terrestrial dissolved organic matter (DOM) whereas an increased ratio of 1.2–1.5 was observed during the remineralization of the Baltic Sea DOM. This indicates that tDOM consists of carbohydrate-like compounds. The higher O₂ demand for the mineralization of mDOM can be explained by a higher proportion of lipid-like compounds and by nitrification.

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1. Introduction

Dissolved organic matter (DOM) in seawater is one of the largest reservoirs of organic carbon on Earth being of the same magnitude as atmospheric CO₂ (Emerson and Hedges, 2008). DOM is a complex mixture of organic compounds, such as amino-acids, peptides, carbohydrates, lipids, lignin, and humic or fulvic substances (Benner, 2002; Nebbioso and Piccolo, 2013). DOM in seawater can be autochthonous, originating from breakdown and excretion processes of marine organisms, or allochthonous, supplied mainly by rivers and groundwater seepage. The continuous reworking by photochemical and microbial transformations changes the composition of DOM and its biochemical availability. DOM also modifies light availability in seawater, interacts with trace metals, radionuclides and organic pollutants being responsible for their transport and transformations (Benner et al., 1992; Maciejewska and Pempkowiak, 2014; Ogawa and Tanoue, 2003; Szymczycha et al., 2014). Through its functional groups having acidic properties it

furthermore affects directly the marine acid–base system (Kuliński et al., 2014; Ulfsbo et al., 2015). Finally, DOM is an important component of the biogeochemical cycles of C, N, P and O. It fuels the microbial loop and is thus considered as additional source of energy and nutrients (Hansell, 2013; Lonborg and Alvarez-Salgado, 2012; Repeta, 2014).

A special attention is given to the transformations of terrestrial dissolved organic carbon (tDOC) in the shelf seas (Hedges et al., 1997; Opsahl and Benner, 1997). Based on the analysis of DOC vs. salinity diagrams, some reports indicate a conservative behavior of tDOC during mixing of river water with seawater (Abril et al., 2002; Dittmar and Kattner, 2003; Kattner et al., 1999). However, possibly the mineralization of tDOC could not be detected in these diagrams because of simultaneous DOC release from estuarine primary production (Alling et al., 2008; Raymond and Bauer, 2001). Opsahl and Benner (1997) estimated that residence time of tDOC is much shorter than that of marine DOC suggesting that tDOC is removed on its way to the open ocean. Removal of tDOC can be biotic (bacterial respiration) or abiotic (photooxidation, flocculation and sorption) (Ogawa and Tanoue, 2003). Bacterial uptake and photooxidation of DOM lead to remineralization of tDOC, which consumes oxygen and releases CO₂, contributing to hypoxia and

* Corresponding author.

E-mail address: kroll@iopan.gda.pl (K. Kuliński).

changes within the carbonate system, respectively (Aarnos et al., 2012; Amon and Benner, 1996; Anderson et al., 2009; Hansell et al., 2004; Ogawa and Tanoue, 2003). Thus, understanding of tDOC transformation dynamics in seawater is especially important in the shelf regions affected by the high inflows of tDOC-rich river water. Biogeochemical and ecosystem models used for simulation of the marine CO₂ system and pH in shelf seas have to include mineralization processes of DOC originating from both terrestrial and marine sources (Lønborg and Alvarez-Salgado, 2012). This requires knowledge about the mineralization rate constants. However, experimental data on DOC mineralization dynamics are still sparse.

The Baltic Sea is a semi-enclosed shelf sea with a mean river runoff of 428 km³ yr⁻¹, which constitutes almost 2% of the total water volume of the sea. The rivers flowing into the Baltic Sea drain an area that is more than four times larger than that of the sea itself. Kuliński and Pempkowiak (2011) reported that rivers are the major source of organic carbon to the Baltic Sea. It amounts to $341 \pm 64 \cdot 10^9$ mol °C yr⁻¹ (Kuliński and Pempkowiak, 2011) and the bulk of this flux is believed to be supplied as tDOC (Deutsch et al., 2012; Stepanauskas et al., 2002). The magnitude of this load equals as much as 75% of the sum of organic carbon exported to the North Sea and buried in the sediments (Kuliński and Pempkowiak, 2011; Kuliński et al., 2011). High river runoff and limited water exchange with the North Sea through the shallow and narrow Danish Straits support retention of the terrestrial organic carbon supplied via rivers to the Baltic. However, little is known about its pathways and transformations in the sea, and especially about the dynamics of mineralization processes. This is mostly due to the problems with tracing terrestrial carbon in the Baltic Sea water and distinguishing between effects caused by terrestrial and marine organic matter mineralization (Alling et al., 2008; Deutsch et al., 2012). Based on the assessment of stable isotopes signatures of sulfur (Alling et al., 2008) and carbon (Deutsch et al., 2012) it was shown that residence time of tDOC in different basins of the Baltic is shorter than that of water. Moreover, it was suggested that tDOC removal takes place in the vicinity of the coast, e.g., in the river estuaries during mixing of seawater and freshwater masses (Deutsch et al., 2012). This makes the quantification of the tDOC mineralization even more challenging due to complexity of the estuarine environment.

Since the mineralization of DOC adds CO₂ to the surface water it has a direct effect on the marine acid–base system and may reinforce the acidification caused by increasing atmospheric CO₂, if the input of terrestrial DOC is increasing in a future climate. This effect must be taken into account when simulating the future biogeochemical development of the Baltic Sea. It requires not only a realistic scenario for the release of DOC from soils in the catchment, but also a quantitative understanding and description of the dynamics of the mineralization process that generates CO₂ in seawater. Therefore, with our study we are aiming at:

- the characterization of the DOC stability with respect to its oxidation to CO₂ by defining and quantifying different stability (reactivity) fractions;

- the determination of mineralization rate constants and half-life times that reflect the generation of CO₂;

- assessing differences between terrestrial (tDOC) and DOC encountered in the Baltic Sea (mDOC), and low-molecular and high-molecular weight DOC;

- estimating the oxygen demand for the DOC mineralization.

2. Methods

2.1. Sampling and incubation setup

Samples from rivers Vistula and Oder were taken during a RV Oceania cruise to the southern Baltic Sea in May 2012. The sampling of the Vistula River was performed from rubber boat about 2.5 km inland from the river mouth. The Oder River was sampled directly on board of the RV Oceania at the entrance to the Szczecin Lagoon (Fig. 1) At

both stations 180 L of river water were transferred to pre-cleaned HDPE containers. Samples were immediately filtered onboard through 0.4 μm MN GF5 glass fiber filters (pre-combusted at 450 °C for 8 h). Subsequently the high molecular weight tDOC (HMW-tDOC) was concentrated in the samples using an ultrafiltration technique based on the PALL tangential flow filtration system equipped with 1 kDa molecular weight cut-off membrane (Schwalger and Spitz, 2009). The permeate obtained from the enrichment of HMW-tDOC fraction was used to concentrate the low molecular weight tDOC (LMW-tDOC) using a 0.5 kDa molecular weight cut-off membrane. The tDOC extracts were stored in the dark at 4 °C until beginning of the incubation experiment. To estimate the initial HMW-tDOC concentration in river water, the DOC concentration of the extract obtained after a volume reduction by a factor of two, was determined. The difference to the original DOC concentration then corresponds to the HMW-tDOC concentration in the river water provided that the retention efficiency was 100% for molecules > 1 kDa. It was found that about 5% of the total river water DOC concentration still existed in the permeate of the second filtration step. We assigned this fraction also to the LMW-tDOC of river water, which was thus given by the DOC in the permeate after the first filtration step.

Seawater for the incubation experiment was taken from the Mecklenburg Bight (Fig. 1) after the spring bloom in June 2012. Immediately after delivery to the laboratory it was divided into 5 batches. The samples were not filtered and thus contained also some POC. However, even at the peak of the spring bloom in the Mecklenburg Bight in March the maximum POC production contributes only about 10% to TOC (Schneider et al., 2015). Hence, the influence of the POC mineralization on the TOC mineralization is considered to be negligible.

One batch remained untreated and was used as a control during the experiment. The other four batches were spiked with different LMW-tDOC and HMW-tDOC from both the rivers Oder and Vistula. This resulted in DOC concentrations that were by a factor of 2.5–3.5 higher than that in the original seawater sample (Table 1). Afterwards, each of these 5 batches were further sub-divided into 10 sub-samples (10 separate bottles) which were analyzed individually after a preassigned incubation time. The bottles (500 mL) contained a headspace volume of about 1 mL to allow for thermal expansion of the sample. They were tightly closed and placed in the dark. Incubation was conducted for 188 days at 20 ± 0.5 °C. The samples were daily carefully shaken in order to ensure homogeneous conditions during the incubation. At the beginning ($t = 0$) and after 1, 2, 3, 6, 9, 20, 34, 65, 188 days of the incubation the individual samples were analyzed for total dissolved inorganic carbon (C_T) and O₂ concentrations. Hence, the progress of the DOC mineralization was tracked by the analysis of 10 different samples corresponding to 10 different bottles. These can be considered as replicates which indicate the reproducibility of the mineralization process through the continuity of the decay curves. Due to this procedure, a total of 50 samples were analyzed for total CO₂ and O₂ concentrations. DOC concentrations were measured in the samples only at the beginning of the incubation ($t = 0$).

2.2. Analytical procedures

After the elapsed incubation time for the individual samples, we first determined the oxygen concentrations using the Fibox 3 optode measurement system in combination with an oxygen dipping probe (PreSens Precision Sensing GmbH). The probe was placed for about 20 s into the sample for recording the O₂ partial pressure, pO₂, that yielded the O₂ concentration at the given temperature and salinity. Calibration of the optode measurements was performed by gas-phase calibration. Pure nitrogen gas was used for the zero adjustment whereas measurements of a defined pO₂ were performed with ambient air. The pO₂ of the latter was determined by assuming standard dry atmospheric composition and taking into account the water vapor content of the ambient air. Tests have indicated that this procedure allows for an accuracy/precision of the O₂ measurements of +/- 1%–2%.

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