Carbon Isotopes in DIC trace Submarine Groundwater Discharge and Advective Pore water efflux in Tidal Areas of the southern North Sea

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ABSTRACT

We report results from a study conducted in different tidal basins of the southern North Sea, here with a focus on the Jade Bay and the backbarrier tidal area of Spiekeroog Island. The present study combines the results from several seasonal sampling campaigns that investigated the tidal response of the pelagic carbonate system under different magnitudes of superimposition by mixing processes with fresh waters and *in-situ* transformation processes, like primary production and pelagic respiration. In addition, benthic processes were followed by the analyses of fresh water inlets, as well as intertidal pore waters recovered from short sediment cores. Finally, direct advective pore water efflux from permeable sediments during low tide was considered, too. Both, the concentration and the stable carbon isotope composition of DIC are shown to be valuable tools to follow and interpret the basic processes causing tidal and spatial variations in the pelagic carbonate system of the coastal waters, in particular when combined with parameters like salinity, nutrients and redox-sensitive metal analyses.

INTRODUCTION

The pelagic carbonate system in the southern North Sea may significantly be impacted by the intense biogeochemical processes taking place within the tidal areas of the southern North Sea (e.g., Brasse et al., 1999; Thomas et al., 2009), with only few studies carried out to understand the dynamics in the tidal basins (e.g., Hoppema, 1990; Moore et al., 2011; Winde et al., 2014). The sources for alkalinity (TA) and dissolved inorganic carbonate (DIC) may result from mixing with fresh waters originating from rivers, flood gates, submarine ground water discharge, or benthic-pelagic exchange of pore waters that were modified by oxidation of organic matter and/or methane (Billerbeck et al., 2006; Al-Raei et al., 2009; Moore et al., 2011) and *in-situ* processes. Here, we present results from studies conducted in two tidal basins of the southern North Sea. It was the aim of this study to investigate seasonal and tidal responses of the pelagic carbonate system in the basin without and under superimposition by *in-situ* transformation processes, like primary production and pelagic respiration. Both, the concentration and the stable carbon isotope composition of DIC are shown to be valuable tools to follow and analyze the tidal and spatial variations in the pelagic carbonate system of the tidal coastal waters. The composition of fresh water inlets at the Jade Bay coast as well as pore waters from selected intertidal surface sediments from both basins were investigated as examples for water and DIC sources draining into the basins. Results are evaluated by the combined consideration of mixing and carbon transformation processes, demonstrating that different source-sink contributions are obtained as a function of season.

MATERIALS AND METHODS

Water samples from fresh water inlets, and coastal sediments were taken as described earlier (Al-Raei et al., 2009; Winde et al., 2014). Salinity, temperature and pH were immediately measured. Water aliquots were filtered (0.45 µm membrane filters) for further analyses by ICP-OES/MS (Thermo iCAP 6300 Duo, ElementII) for major and redox-sensitive trace elements, a QuAAtro nutrient analyzer (SEAL Analytical). Analyses of TA and DIC were carried out via potentiometric and coulometric titration, respectively (Winde et al., 2014). The $\delta^{13}C$ values of DIC were measured by means of CF-irmMS using a Thermo Finnigan MAT 253 gas mass spectrometer coupled to a Thermo Gas Bench II via a Thermo Conflo IV split interface.

RESULTS AND DISCUSSION

Seasonal and tidal changes in the carbonate system of a tidal basin.

It has been shown that seasonal and tidal compositional variations occur in the investigation areas that indicate the mixing of North Sea with fresh waters of different sources, superimposed by benthic-pelagic coupling (Moore et al., 2011; Winde et al., 2014). The consideration of seasonal variations, here for the example of the Jade Bay (Figure 1), yields characteristic compositional variations that can be evaluated based a common evaluation of the concentration and stable isotope composition of DIC. Mixing with fresh and pore waters as well as photosynthesis are the dominant processes controlling observed co-variations.

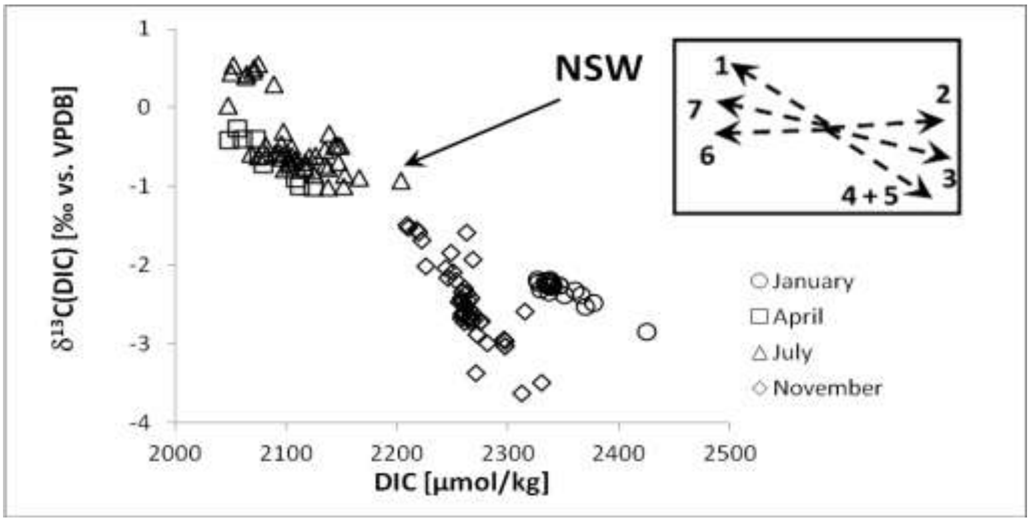

Figure 1a. Co-variations of the concentration and carbon isotopic composition of DIC in the upper water column of the Jade Bay (tidal cycles and transects), southern North Sea during 4 sampling campaigns in 2010. NSW: North Sea (surface) water as an end-member for winter mixing with fresh waters. DIC data from the July campaign were calculated from TA and pH values with CO2SYS (Lewis & Wallace, 1998). Arrows in the small window indicate the processes with potential impact on the pelagic coastal carbonate system according to the concept proposed by Winde et al. (2014), with: 1 Photosynthesis, 2 $CaCO_3$ dissolution, 3 CO_2 invasion, 4 OM mineralization, 5 mixing with anoxic pore water/fresh water, 6 $CaCO_3$ mineralization, 7 CO_2 degassing. The slope for #5 strongly depends on the composition of the pore/fresh water mixing compound. Winter data are taken from Winde et al. (2014). Fresh water inlets: October (DIC: 1373-6542 µmol/kg; $\delta^{13}C$: -14.9 to -16.1‰ VPDB; Winde et al., 2014), May (DIC: 1358-6279 µmol/kg; $\delta^{13}C$: -3.4 to -10.9‰ VPDB).

Efflux of anoxic pore waters from an intertidal sand plate.

Outflow of nutrient enriched anoxic pore waters has been shown for intertidal sand plates in the backbarrier tidal areas of the southern North Sea, a process that is driven by pressure differences during low tide and may impact the composition of the water column to extends depending on season and hydrological conditions (Billerbeck et al., 2006; Al-Raei et al., 2009; Dellwig et al., 2007; Moore et al., 2011). This is a further example for intense benthic-pelagic coupling providing an additional source for DIC and TA, besides nutrients and redox-sensitive elements.

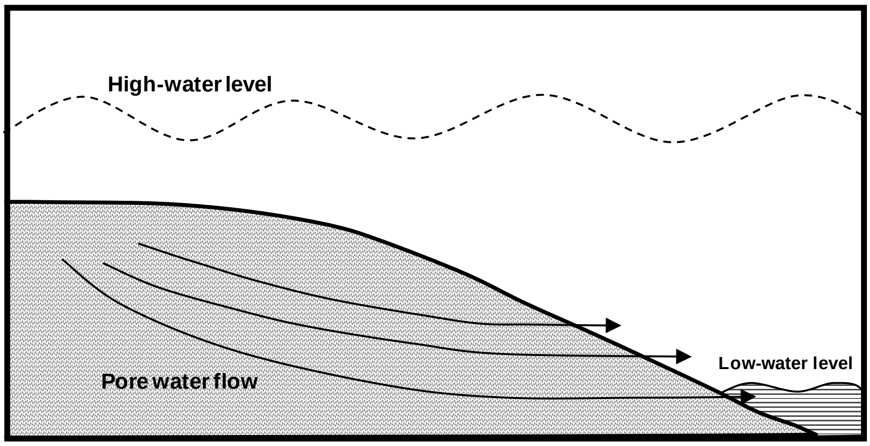

Figure 2a. A model scheme for the liberation of anoxic pore waters from permeable intertidal sands during low tide (modified after Billerbeck et al., 2006).

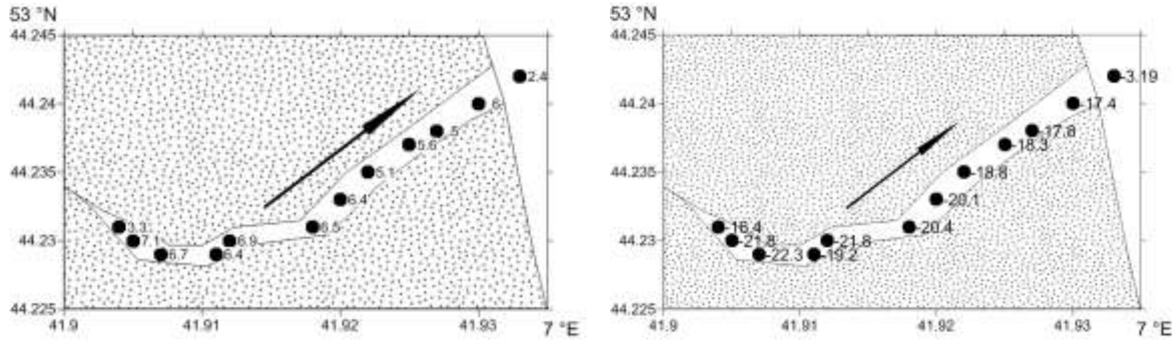

Figure 2b. Efflux of anoxic pore water from the Janssand (sand plate in the backbarrier tidal area of Spiekeroog Island) during low tide (31st October 2010) as shown by enhanced concentrations (left; in [mM]) of isotopically light (right; in [‰ vs. VPDB]) DIC, and dissolved sulfide and redox-sensitive trace metals (data not shown). Arrow: Flow direction towards the main tidal channel (right side). The enhancement of isotopically light DIC is mainly due to the oxidation of biogenic methane in the sediments (Böttcher et al., 2007).

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