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The influence of dissolved organic matter on the acid-base system of the Baltic Sea: A pilot study

Karol Kulinski (1), Bernd Schneider (2), Karoline Hammer (2), and Detlef Schulz-Bull (2)

(1) Institute of Oceanology PAS, Marine Biogeochemistry, Sopot, Poland (kroll@iopan.gda.pl), (2) Leibniz Institute for Baltic Sea Research Warnemuende

To assess the influence of dissolved organic matter (DOM) on the acid-base system of the Baltic Sea, 19 stations along the salinity gradient from Mecklenburg Bight to the Bothnian Bay were sampled in November 2011 for total alkalinity (AT), total inorganic carbon concentration (CT), partial pressure of CO_2 (pCO_2), and pH. Based on these data, an organic alkalinity contribution (Aorg) was determined, defined as the difference between measured AT and the inorganic alkalinity calculated from CT and pH and/or CT and pCO_2. Aorg was in the range of 22–58 μmol kg-1, corresponding to 1.5–3.5% of AT. The method to determine Aorg was validated in an experiment performed on DOM-enriched river water samples collected from the mouths of the Vistula and Oder Rivers in May 2012. The Aorg increase determined in that experiment correlated directly with the increase of DOC concentration caused by enrichment of the >1 kDa DOM fraction. To examine the effect of Aorg on calculations of the marine CO_2 system, the pCO_2 and pH values measured in Baltic Sea water were compared with calculated values that were based on the measured alkalinity and another variable of the CO_2 system, but ignored the existence of Aorg. Large differences between measured and calculated pCO_2 and pH were obtained when the computations were based on AT and CT. The calculated pCO_2 was 27–56% lower than the measured values whereas the calculated pH was overestimated by more than 0.4 pH units. Since biogeochemical models are based on the transport and transformations of AT and CT, the acid-base properties of DOM should be included in calculations of the CO_2 system in DOM-rich basins like the Baltic Sea. In view of our limited knowledge about the composition and acid/base properties of DOM, this is best achieved using a bulk dissociation constant, KDOM, that represents all weakly acidic functional groups present in DOM. Our preliminary results indicated that the bulk KDOM in the Baltic Sea is 2.94•10-8 mol kg-1. Although this KDOM has no thermodynamic meaning, it can be a useful tool in numerical studies as it allows an approximation of Aorg in seawater.