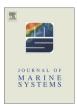
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Dissolved organic matter in the Baltic Sea

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ABSTRACT

Several factors highlight the importance of dissolved organic matter (DOM) in coastal ecosystems such as the Baltic Sea: 1) DOM is the main energy source for heterotrophic bacteria in surface waters, thus contributing to the productivity and trophic state of bodies of water. 2) DOM functions as a nutrient source: in the Baltic Sea, more than one-fourth of the bioavailable nutrients can occur in the dissolved organic form in riverine inputs and in surface water during summer. Thus, DOM also supports primary production, both directly (osmotrophy) and indirectly (via remineralization). 3) Flocculation and subsequent deposition of terrestrial DOM within river estuaries may contribute to production and oxygen consumption in coastal sediments. 4) Chromophoric DOM, which is one of the major absorbers of light entering the Baltic Sea, contributes highly to water color, thus affecting the photosynthetic depth as well as recreational value of the Baltic Sea. Despite its large-scale importance to the Baltic Sea ecosystem, DOM has been of minor interest compared with inorganic nutrient loadings. Information on the concentrations and dynamics of DOM in the Baltic Sea has accumulated since the late 1990s, but it is still sporadic. This review provides a coherent view of the current understanding of DOM dynamics in the Baltic Sea.

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1. Introduction

The Baltic Sea, with its high input of river water from a wide catchment area, receives a substantial proportion of its dissolved organic matter (DOM) from terrestrial sources (Deutsch et al., 2012). Terrestrial DOM (tDOM) transported by streams and rivers represents an important pathway of carbon (C) and nutrients from terrestrial to aquatic ecosystems. The input of DOM has consequences in food web structure, since it is a source of energy and nutrients for bacteria (Sandberg et al., 2004). It may also promote the growth of dinoflagellates (Purina et al., 2004), thus affecting autochthonous production of organic matter. DOM in natural waters is both a natural background source of acidity and a pH buffer in low-alkalinity waters, and thus affects the acidbase balance in surface waters. It also plays an important role in the transport and availability of trace metals and contaminants; a significant, though highly variable, part of nutrient trace metals (e.g. iron (Fe), copper (Cu) and nickel (Ni)) as well as non-nutrient trace metals (e.g. aluminium (Al), mercury (Hg) and lead (Pb)) in the dissolved phase, is bound in organic ligands in coastal and open-sea waters (summarized by Wells, 2002). The binding of trace metals to organic ligands can prevent their adsorption to particles and subsequent sinking, but, on the other hand, flocculation of these complexes may at times be significant and cause a drawdown of the trace metals from the surface water (Wells, 2002). The optical properties of DOM have major implications for ecosystem functioning (Kothawala et al., 2014). The chromophoric DOM (CDOM) compounds that absorb ultraviolet (UV) and visible light play a dominant role in the light regime, allowing less light to penetrate into water (Dupont and Aksnes, 2013). The transparency and heat budgets of surface waters are thus modified and partly controlled by DOM. In this way DOM has an indirect effect on the primary producers. Sandberg et al. (2004) suggested that this contributes to the low phytoplankton production in the Bothnian Bay, where riverine inputs of tDOM are high. Thus, DOM plays a multiple system-wide role in the ecology of the Baltic Sea. This has been recognized by the Helsinki Commission (HELCOM, 2010) as assigning inputs of organic matter from rivers high status regarding their potential pressures on the Baltic Sea.

This review compiles the data published from the Baltic Sea. It begins at the catchment and ends in giving up-to-date budgets on allochthonous and autochthonous DOM. We attempt to summarize our knowledge of all aspects of abiotic and biotic transformation and utilization of DOM and its major elements (C, nitrogen (N) and phosphorus (P)). The second specific question is how the available information can be summarized to describe the specific conditions in different Baltic Sea areas and if any trends in concentrations can be found. We have given an account of recent work, as well as pinpointed the gaps in our knowledge. This review highlights the importance of DOM as one of the major pressures in the Baltic Sea ecosystem management, improving the understanding of DOM sources and its fate in the Baltic Sea with implications for ecosystem modeling and system analysis.

2. Spatial distribution of DOM

2.1. Distribution of DOC

In the Baltic Sea (Fig. 1), studies of dissolved organic carbon (DOC) concentrations were already conducted in the 1970s and early 1980s, but information on DOC concentrations began to accumulate more rapidly only in the 1990s. The number of DOC studies has increased during the last decade, but information on DOC concentrations and dynamics in the Baltic Sea is still sporadic. In the majority of the studies DOC has been measured with high-temperature oxidation, which is the most widely used method in DOC analytics. Few investigations have used persulfate oxidation (Jurkowskis et al., 1976; Kuliński and Pempkowiak, 2008; Kulinski et al., 2011; Pempkowiak et al., 1984), which gave comparable concentrations but higher scatter than high-temperature oxidation in an intercalibration of DOC measurement (Sharp et al., 2002). Two studies reported total organic carbon (TOC) instead of DOC (Table 1; Perttilä and Tervo, 1979; Wedborg et al., 1994). Since DOC concentrations exceed those of particulate organic carbon (POC) by an average of 48-fold in the Baltic Proper (Nausch et al., 2008), and the DOC stock has been modeled to exceed that of POC by 100-fold in the Baltic Sea (Gusstafsson et al., 2014), we presumed that the DOC concentrations are roughly equal to those of TOC.

In the open-sea surface water of the Baltic Sea, concentrations of DOC range from about 260 to about 480 $\mu mol\ C\ l^{-1}$ (Table 1), exceeding those in the surface water (top 100 m) of the Atlantic Ocean approximately 3–6 fold (about 50–80 $\mu mol\ C\ l^{-1}$; Carlson et al., 2010). In the open ocean, almost all of the DOM ultimately derives from local phytoplankton production, whereas in coastal areas allochthonous loading contributes extensively to DOM concentrations. DOC concentrations of 290–1900 $\mu mol\ C\ l^{-1}$ in the rivers entering the Baltic Sea are clearly higher than those in the Baltic Sea itself (Fleming-Lehtinen et al., 2014; Räike et al., 2012; Stepanauskas et al., 2002). Accordingly, the DOC concentrations in the Baltic Sea are generally higher in areas with high terrestrial influence. Strong temporal variation in DOC concentrations and sporadic data impede examination of spatial and seasonal trends, but some features are nevertheless prominent.

2.1.1. Gulf of Finland

In the open-sea water of the western Gulf of Finland, DOC concentrations vary widely (290–480 $\mu mol~C~l^{-1}$; Fig. 2). The concentrations are generally about 50 $\mu mol~C~l^{-1}$ above those in the Baltic Proper (Fig. 2, Table 1), probably due to higher allochthonous inputs. The DOC concentrations in the open-sea area increase eastward from the mouth of the Gulf (Hoikkala et al., 2012), and DOC concentrations in the Neva Bay are over 200 $\mu mol~C~l^{-1}$ (50–60%) higher than those in the western Gulf of Finland (Aarnos et al., 2012). The gradient is probably affected by discharge into the Neva Bay, mainly from the Neva River the largest river draining into the Baltic Sea (discharge 2500 $m^3~s^{-1}$). Due to the anticlockwise circulation of the water mass, the DOC loads from the

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