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Dissolved organic phosphorus: An indicator of organic matter turnover?

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ABSTRACT

Seasonal and interannual variations of dissolved organic phosphorus (DOP) are analysed for five stations in the Dutch Wadden Sea (southern Wadden Sea, 1991–2007) and one station in the northern Wadden Sea (List tidal basin near Sylt, 2000–2009). A clear seasonal cycle is observed with low winter DOP values of around 0.1–0.2 μM and a summer maximum of up to 1.6 μM. Mean summer DOP concentrations show a decreasing trend in line with a decrease in the eutrophication level of the Wadden Sea. Regional differences exist in the mean summer DOP levels with highest values in the eastern part of the Dutch Wadden Sea and lowest values in the northern Wadden Sea near Sylt. A regional comparison for the years 2000–2007 shows that average summer DOP values are correlated with average summer phytoplankton chlorophyll-*a* (proxy for biomass) and autumn ammonium concentrations suggesting that highest DOP values are found in those regions where highest phytoplankton production and highest autumn remineralisation occurs. We conclude that the summer DOP values may be used as a useful indicator of regional differences and is worth to further investigate as indicator of interannual trends in organic matter turnover in the Wadden Sea.

1. Introduction

The Wadden Sea receives a significant share of the nutrients discharged by European continental rivers into the North Sea. At least three pathways are involved: direct discharges by rivers debouching directly into the Wadden Sea like the IJssel (through Lake IJsselmeer), Ems, Weser and Elbe, atmospheric input and the import of organic matter produced in the North Sea outside of the Wadden Sea. According to Postma (1984) this import is one of the characteristic features of the organic matter dynamics in the Wadden Sea. Carbon budgets for the Wadden Sea support its heterotrophy (Hoppema, 1991; van Beusekom et al., 1999) and the import of organic matter from the North Sea is suggested to be a major driver of Wadden Sea eutrophication (van Beusekom et al., 2001; van Beusekom and de Jonge, 2002).

The various nutrient sources involved in the eutrophication of the Wadden Sea hamper a straightforward quantification of Wadden Sea nutrient budgets. The major riverine nutrient sources are now routinely monitored and their nutrient loads quantified reasonably well (e.g. Radach and Patsch, 2007). The quantification of the organic matter and nutrient loads due to the import of suspended matter and associated organic matter and nutrients, however, is still a challenge. Due to strong tidal currents large amounts of dissolved and particulate material are exchanged between the Wadden Sea and the North Sea and only a small portion remains within the Wadden Sea (e.g. Cadée, 1982). Carbon budgets support the importance of organic matter. The effort, however, involved in gathering the necessary data like estimates of primary and secondary production and remineralisation rates and the inaccuracy involved do not make these budgets useful instruments to resolve any changes in the spatial and temporal organic matter turnover (van Beusekom et al., 1999).

Eutrophication has been defined in quite different ways. From the carbon perspective it can be defined as an increased turnover of organic matter (Nixon, 1995). Carbon budgets are tedious and the uncertainty involved may preclude detailed conclusions (e.g. van Beusekom et al., 1999). Therefore proxies have to be developed that inform on the past and present eutrophication status of a specific area. Van Beusekom and de Jonge (2002) demonstrated that in the Dutch Wadden Sea the sum of the autumn values of NH_4^+ and NO_2^- were higher during wet years (with a relatively high riverine nutrient load) than during dry years (with a relatively low load). A multiple regression analysis including autumn temperature and autumn chlorophyll levels showed a significant correlation

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with riverine total nitrogen (TN) loads by the rivers Rhine and Maas. In the northern Wadden Sea, mean summer phytoplankton chlorophyll-*a* mass correlated significantly with the TN loads by the rivers Weser and Elbe during 1984–2006 (van Beusekom et al., 2009a). A recent assessment of the Wadden Sea eutrophication status showed that summer phytoplankton chlorophyll-*a* (mean of May–September) can be used as a general indicator of the Wadden Sea eutrophication status: most of the available long time series (>20 years) show a significant correlation between summer phytoplankton chlorophyll-*a* and riverine TN input (van Beusekom et al., 2009b). Since the mid 1980's the TN and TP loads of the main rivers influencing the Wadden Sea are decreasing (e.g. Radach and Patsch, 2007) and a general decrease in phytoplankton chlorophyll-*a* and productivity is observed (Cadée and Hegeman, 2002; van Beusekom et al., 2009a, b).

Both proxies mentioned above (summer chlorophyll-*a* and autumn $NH_4^+ + NO_2^-$) are correlated and as such proved to be useful in assessing both regional differences and temporal trends in Wadden Sea eutrophication (van Beusekom et al., 2009b). However, given the importance of organic matter import from the adjacent off-shore North Sea for the organic matter turnover in the Wadden Sea, a measure that more directly reflects the level of organic matter turnover would greatly enhance our understanding of the Wadden Sea and possibly enable a more accurate assessment of relative differences among regions and between years. For instance, it is feasible, that phytoplankton chlorophyll-*a* reflects not only the nutrient conditions. Variations in light (e.g. Colijn, 1982; Cloern, 1999) or grazing (Hansen et al., 1993; Loebl and van Beusekom, 2008) also affect phytoplankton biomass. Here we explore the use of dissolved organic nutrients and more specifically dissolved organic phosphorus (DOP) as a possible indicator of organic matter turnover in the Wadden Sea. We will not argue that phytoplankton directly influences DOP. Rather, we consider DOP as an indicator of total organic matter turnover in the Wadden Sea without assigning a specific source to it, being the sediment or the water column.

DOP is not a regular part of most monitoring programs and limited information on its regional and temporal dynamics is available. Postma (1954) explored the seasonal cycle of phosphorus in the Western Dutch Wadden Sea by measuring DIP, DOP and total phosphorus and observed only a slight seasonal cycle in DOP with highest concentrations during winter and an annual mean of about 0.3 μM (recalculated by de Jonge and Postma, 1974). During 1970–1972, similar concentrations were observed despite significantly increased riverine phosphorus loads (de Jonge and Postma, 1974). Brockmann et al. (1999) addressed dissolved nutrient dynamics in the German Wadden Sea and observed very low DOP concentration in the Wadden Sea contributing less than 10% to total P concentrations of about 2 μM being mostly near the detection limit of DOP. Since then, little attention has been given to DOP behaviour in the Wadden Sea and no information is available on its regional and temporal dynamics in the Wadden Sea. It is an open question, whether sediments or suspended matter (and suspended phytoplankton detritus) are the main sources. As a first approximation we will assume that both sources are of equal importance. Heip et al. (1995) showed that in very shallow temperate coastal zones benthic and pelagic remineralisation are of equal importance. In contrast to our limited knowledge on DOP more is known about the DIP cycle in coastal waters. Iron-oxihydroxides play a dominant role as a DIP buffer under oxic conditions or a source under anoxic conditions (Jensen et al., 1995). de Jonge and Postma (1974) noted a strong increase in the DIP seasonal cycle between 1950 and 1970 due to an enhanced import of particulate phosphorus from the North Sea and an enhanced release from Wadden Sea sediments. It is, however, still questioned what the drivers are for the observed variation in DIP. Since the mid 1980's DIP concentrations in the Wadden Sea decrease again (e.g. de Jonge, 1997) but whether and how DOP concentrations have changed in response to the decreasing riverine Phosphorus loads remains to date unknown.

In the present paper we present data on DOP in the northern Wadden Sea measured since 2000 as part of a weekly long-term study started in 1984 (e.g. Martens and van Beusekom, 2008; van Beusekom et al., 2009a). We will compare our results with DOP data measured monthly since 1991 as part of the Dutch monitoring program in the Dutch Wadden Sea and explore the value of DOP as a possible indicator of the Wadden Sea eutrophication status.

2. Material and methods

2.1. Area description

The Wadden Sea is the world largest coherent tidal flat system in the temperate world (Reise et al., 2010). It stretches about 400 km along the Dutch, German and Danish North Sea coast (Fig. 1). Because of the interaction of different amphidromic systems in the North Sea, the tidal range is about 1.5 m at the northern and southern end increasing to about 3.5 m in the central parts near the estuaries of the rivers Weser and Elbe. Where the tidal range does not exceed 2.5 m the tidal flats are protected from the North Sea by barrier islands. Average depth is about 2–3 m and during low tide about 50% of the area emerges. Sediments are mostly sandy, but in areas protected from strong wind and currents, mudflats and salt marshes may develop. Salinity is around 30 in most areas but can be lower in the vicinity of estuaries and near sluices used for fresh water discharge.

2.2. Sylt time series (List tidal basin)

Twice a week, water samples from about 1 m below the surface are taken from a ship with a Niskin type water sampler in one of the main tidal channels and at a nearby subtidal station (see van Beusekom et al., 2009a) independent from the tidal phase. Parameters measured routinely include salinity, temperature, suspended matter, inorganic nutrients and phytoplankton chlorophyll-*a*. In the laboratory the water samples are filtered through pre-combusted GF/C glassfibre filters (1 h at 450 °C) and stored frozen at −20 °C until analysis. Total dissolved nutrients were measured after digesting the dissolved organic matter using the alkaline peroxidisulfate method (Grasshoff et al., 1983). DOP was calculated by subtracting dissolved inorganic phosphorus (DIP) from total

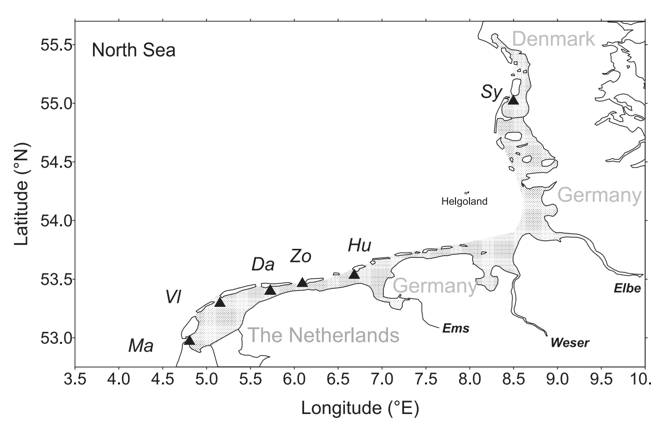

Fig. 1. Map of the Wadden Sea showing the position of the time series stations (triangles) in the Dutch Wadden Sea and in the List tidal basin (Sylt, northern German Wadden Sea). Ma: Marsdiep Noord, Vl: Vliestroom, Da: Dantziggat, Hu: Huibertgat Oost, Sy: Sylt (List tidal basin).