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Setting background nutrient levels for coastal waters with oceanic influences

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ABSTRACT

Nutrient enrichment of coastal water bodies as a result of human activities can lead to ecological changes. As part of a strategy to monitor such changes and detect potential eutrophication, samples were collected during research cruises conducted around the Scottish coast each January over the period 2007–2013. Data were obtained for total oxidised nitrogen (TOxN; nitrite and nitrate), phosphate and silicate, and incorporated into data-driven spatial models. Spatial averages in defined sea areas were calculated for each year in order to study inter-annual variability and systematic trends over time. Variation between some years was found to be significant ($p < 0.05$) but no evidence was found for any trends over the time period studied. This may have been due to the relatively short time series considered here. Modelled distributions were developed using data from groups of years (2007–2009, 2010–2011 and 2012–2013) and compared to the OSPAR Ecological Quality Objectives (EcoQOs) for dissolved inorganic nitrogen (DIN; the concentration of TOxN and ammonia), the ratio of DIN to dissolved inorganic phosphorous (N/P) and the ratio of DIN to dissolved silicate (N/S). In these three models, TOxN was below the offshore background concentration of 10 μM (12 μM at coastal locations) over more than 50% of the modelled area while N/S exceeded the upper assessment criterion of 2 over more than 50% of the modelled area. In the 2007–2009 model, N/P was below the background ratio (16) over the entire modelled area. In the 2010–2011 model the N/P ratio exceeded the background in 91% of the modelled area but remained below the upper assessment criterion (24). Scottish shelf sea waters were found to be depleted in TOxN relative to oceanic waters. This was not accounted for in the development of background values for the OSPAR EcoQOs so new estimates of these background values were derived. The implications of these results for setting reasonable background nutrient levels when the relationship between oceanic and coastal nutrient compositions is complex are discussed.

1. Introduction

The availability of inorganic nutrients is often the limiting factor on the growth of primary producers in the marine environment. Thus, the abundance and composition of nutrients are driving forces governing the distribution of phytoplankton. Three of the most commonly limiting nutrients are dissolved inorganic nitrogen (DIN), of which nitrate is the most abundant reactive inorganic form; dissolved inorganic phosphorus (DIP), primarily assimilated as phosphate, and dissolved silicate (DSi), found mainly as silicic acid (H_4SiO_4) and used by diatoms to synthesise their cell walls. Approximate average ratios for these nutrients in organisms are given by their Redfield ratios (Redfield, 1958) of 16:1:16 for N:P:Si, and these ratios tend to closely match the average composition of nutrients in seawater. Individual species may have elemental stoichiometries which differ markedly from the canonical Redfield values (Arrigo, 2005), implying that certain plankton species may be better poised to react to a given change in nutrient composition than others.

Human activities, such as agriculture, sewage treatment and fossil fuel combustion, have been responsible for altering global marine nutrient cycles, particularly in estuarine and coastal areas (Artioli et al., 2008; Duce et al., 2008). Eutrophication, as an undesirable consequence of this, has been recognised as a cause for global concern (Cloern, 2001). It is manifest as increased incidences of algal blooms, including harmful or toxic algae (Heisler et al., 2008), and in shifts in the species composition of plankton

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populations (Tilman, 1977). In Europe, concern over the potential for harmful eutrophication has led to the regular monitoring of nutrient concentrations in marine waters. In the OSPAR (Olso & Paris Regional Sea Convention) region, covering the north-western European seas and extending into the NE Atlantic Ocean, Ecological Quality Objectives (EcoQOs) have been developed to provide a consistent basis for the assessment of eutrophication status across the region. Values below the lower EcoQO (background concentration or ratio) are deemed to be at natural background levels; those exceeding the upper assessment criteria are deemed elevated, posing an unacceptable risk of ecological effect. A difficulty with this approach is the derivation of suitable background concentrations given the lack of long-term time series of nutrient concentrations and the likely spatial and temporal variability of nutrients from natural sources (Painting et al., 2005). In addition to the assessment of nutrient concentrations, the OSPAR Eutrophication Strategy requires the assessment of direct effects, such as chlorophyll levels, and indirect effects such as oxygen deficiency and fish kills. An area will only be defined as a problem area if any nutrient enrichment is also accompanied by direct and/or indirect effects.

In European waters, monitoring is also required under the Marine Strategy Framework Directive (MSFD) of the EU. Within this framework, Descriptor 5 ('Human-induced eutrophication is minimised, especially adverse effects thereof, such as losses in biodiversity, ecosystem degradation, harmful algal blooms and oxygen deficiency in bottom waters') sets out qualitatively the criteria against which Good Environmental Status (GES) with respect to eutrophication should be assessed. In the UK, a two-tiered approach will be used for Descriptor 5 targets and indicators. In areas designated non-problem under the OSPAR Common Procedure (OSPAR, 2013) there should be no increase in the assessed DIN or DIP concentration resulting from anthropogenic nutrient input. In OSPAR problem areas the UK MSFD target is 'for a downward trend in DIN and DIP resulting from decreasing anthropogenic nutrient input over a 10 year period'. Progress towards these targets is to be assessed using data from periodic surveys (at least once per MSFD reporting cycle of 6 years).

The monitoring of nutrients in coastal waters is also required under several EU Directives including the Water Framework Directive (WFD). The WFD will require the quality of water bodies to be categorised as High, Good, Moderate, Poor or Bad. Nutrient concentrations are amongst the physio-chemical quality elements that are required to describe water quality. To achieve a High status, nutrient levels must be within background ranges. The target date for achieving a Good or High status for all water bodies is 2015.

Continental seas around Scotland are typical of north-west European shelf seas, which tend to be stratified during the summer, except where strong tidal currents prevent stratification. However, this stratification breaks down during the winter, allowing the mixing of nutrients from deeper water into the surface layer. Low light intensities and high turbulence ensure that phytoplankton numbers are minimal during the winter so nutrients tend to accumulate, reaching a maximum prior to the return of stratification and the spring bloom. Winter nutrient concentrations set an upper limit on yearly primary production, particularly in offshore areas. The lack of nutrient uptake by phytoplankton means that nutrient distributions more closely reflect those of their sources. This paper assesses the winter nutrient distribution around Scotland relative to the objectives set by the OSPAR EcoQOs and MSFD Descriptor 5. With a low population density and an oceanic influence, conditions and pressures in Scottish waters may be different to those of other countries around the North Sea. However, an improved understanding of the nutrient distribution and trends in Scottish waters will aid in understanding the nutrient dynamics and ecosystem functioning across the north-west European shelf seas.

2. Materials and methods

2.1. Study area

Samples were collected from the continental shelf seas around Scotland (Fig. 1), from the North Sea and from the region extending up to the shelf break to the west of the Outer Hebrides and the north of Shetland. The physical oceanography has been described in detail elsewhere (Otto et al., 1990) but a short summary is presented below. The northward transport of warm, saline waters in the Slope Current to the west of the Hebrides has limited exchange across the shelf edge into the Malin Sea (Burrows and Thorpe, 1999; Pingree et al., 1999; Huthnance et al., 2009). Oceanic water from the Atlantic enters the North Sea by the Fair Isle Current (between Orkney and Shetland) and through the Atlantic inflow to the east of Shetland (Burrows and Thorpe, 1999). This manifests in a more oceanic characteristic in the water masses east of Shetland and in Fladen (Turrell, 1992; Turrell et al., 1996). The Scottish Coastal Current may be found closer to the coastline on the shelf. This current transports water of a more coastal nature northwards from the Irish Sea through the Minches (the straits separating the Outer Hebrides from mainland Scotland) and around Scotland into the North Sea (McCubbin et al., 2002).

With the notable exception of the Clyde catchment, which includes Glasgow (Scotland's largest city), rivers on the west coast of Scotland drain small catchments with low population densities and low levels of industrial and agricultural activity. The Scottish east coast is more heavily populated, particularly towards the south between Dundee and Edinburgh, and subject to greater agricultural and industrial activities.

2.2. Sample collection and storage

Surface water samples ($\sim$4.5 m) were collected from the non-toxic water supply at regular intervals during annual January cruises by the vessel MRV *Scotia* from 2007 to 2013 (Fig. 1). Cruises had been conducted annually from 2001 but, due to a change in analytical technique in 2006, this paper considers only the results from 2007 onwards. The earlier data are presented in Rose et al. (2009). From 2007 to 2009 samples were collected every 15 min along the cruise track while from 2010 onwards they were collected at 30 min intervals. Samples were analysed at sea within 10 h of collection except for those from the 2010, 2011 and 2012 cruises, which were immediately frozen following collection stored and analysed later in an onshore laboratory. The cruise tracks were dictated by the need to collect biota and sediment samples, and varied considerably between years. There was no pre-treatment of samples prior to analysis. Stored samples were split into sub-samples: one, to be analysed for phosphate and TOxN, was stored in a glass bottle at -20 °C and allowed to thaw for 24 h before analysis; a second, to be analysed for silicate, was stored in a plastic test tube at -20 °C and allowed to thaw for 48 h, to allow for depolymerisation, before analysis. Temperature and salinity measurements were recorded at 1 min intervals, at a depth of $\sim$4.5 m, using a Sea-Bird thermosalinograph (TSG). The salinity measurements were then calibrated using salinity measurements from bottled samples determined using a Guildline Portasal Salinometer.

2.3. Determination of nutrients

Most samples were analysed for DIP, total oxidised nitrogen (TOxN: nitrate plus nitrite), and DSi by colorimetry using a Bran and Luebbe QuAAtro continuous flow analysis (CFA) system based on