Deep-Sea Research I 112 (2016) 113–122

Contents lists available at ScienceDirect

Deep-Sea Research I

journal homepage: www.elsevier.com/locate/dsri

Depletion of oxygen, nitrate and nitrite in the Peruvian oxygen minimum zone cause an imbalance of benthic nitrogen fluxes

S. Sommer[a,*], J. Gier[a], T. Treude[b], U. Lomnitz[a], M. Dengler[a], J. Cardich[c], A.W. Dale[a]

[a] GEOMAR Helmholtz Centre for Ocean Research Kiel, Wischhofstrasse 1-3, 24148 Kiel, Germany
[b] Department of Earth, Planetary & Space Science and Atmospheric and Oceanic Sciences, University of California, 595 Charles E. Young Drive East, Los Angeles, CA 90095, USA
[c] Department of Geochemistry, Universidade Federal Fluminense, Niterói, Rio de Janeiro 24020-150, Brazil

ARTICLE INFO

Article history:
Received 6 August 2015
Received in revised form
2 March 2016
Accepted 5 March 2016
Available online 9 March 2016

Keywords:
Benthic nitrogen cycle
Hypoxia
Oxygen minimum zone
Sulphur bacteria
Sulphidic event
Peru

ABSTRACT

Oxygen minimum zones (OMZ) are key regions for fixed nitrogen loss in both the sediments and the water column. During this study, the benthic contribution to N cycling was investigated at ten sites along a depth transect (74–989 m) across the Peruvian OMZ at 12°S. O_2 levels were below detection limit down to ~500 m. Benthic fluxes of N_2, NO_3^-, NO_2^-, NH_4^+, H_2S and O_2 were measured using benthic landers. Flux measurements on the shelf were made under extreme geochemical conditions consisting of a lack of O_2, NO_3^- and NO_2^- in the bottom water and elevated seafloor sulphide release. These particular conditions were associated with a large imbalance in the benthic nitrogen cycle. The sediments on the shelf were densely covered by filamentous sulphur bacteria *Thioploca*, and were identified as major recycling sites for DIN releasing high amounts of NH_4^+ up to 21.2 mmol $m^{-2}\,d^{-1}$ that were far in excess of NH_4^+ release by ammonification. This difference was attributed to dissimilatory nitrate (or nitrite) reduction to ammonium (DNRA) that was partly being sustained by NO_3^- stored within the sulphur oxidizing bacteria. Sediments within the core of the OMZ (ca. 200–400 m) also displayed an excess flux of N of 3.5 mmol $m^{-2}\,d^{-1}$ mainly as N_2. Benthic nitrogen and sulphur cycling in the Peruvian OMZ appears to be particularly susceptible to bottom water fluctuations in O_2, NO_3^- and NO_2^-, and may accelerate the onset of pelagic euxinia when NO_3^- and NO_2^- become depleted.

1. Introduction

A globally significant proportion of fixed nitrogen (N) loss proceeds in the relatively restricted marine areas known as ocean oxygen minimum zones (OMZ) due to the redox-sensitivity of N cycling processes (Gruber, 2004). Quantitative knowledge of the balance between fixed N source, sink and recycling pathways is required to understand feedbacks between surface water primary productivity and the maintenance or even spreading of OMZs (Stramma et al., 2008). N source/sink processes in the sediments form an integral part of the ecological status of OMZs, and of the oceans in general (Kalvelage et al., 2013; Devol, 2015).

The first in situ N flux measurements in the most productive upwelling system in the world off Peru (Bohlen et al., 2011) challenged the common understanding that shelf and slope sediments in high–nitrate–low–oxygen environments are mainly sinks for nitrate (NO_3^-) and nitrite (NO_2^-) by heterotrophic denitrification (Berelson et al., 1987; Devol and Christensen, 1993; Middelburg et al., 1996; Hartnett and Devol, 2003; Woulds et al., 2009). By combining flux measurements with pore water modelling, Bohlen et al. (2011) identified the anoxic Peruvian shelf and upper slope sediments at 11°S as important recycling sites for dissolved inorganic nitrogen (DIN, defined as $NO_3^- + NO_2^- + NH_4^+$(ammonium)). A major proportion of the total $NO_3^- + NO_2^-$ uptake was channelled into dissimilatory nitrate reduction to ammonium (DNRA), producing NH_4^+ as an end product rather than N_2. DNRA contributed up to 80% to the total benthic NH_4^+ release, with the remainder from organic nitrogen degradation (ammonification). In contrast to denitrification and anammox, DNRA retains DIN in the ecosystem, thereby opposing the self-cleansing effect of N loss via denitrification or anammox (Zopfi et al., 2001). The NH_4^+ released from the seabed is hypothesized to strongly contribute to pelagic anammox (Lam et al., 2009; Kalvelage et al., 2013) and, possibly, phototrophic primary production.

DNRA in Peruvian sediments is carried out by filamentous and nitrate-storing sulphur oxidizing chemolithotrophs belonging to the genera *Beggiatoa* and *Thioploca* (Jørgensen and Nelson, 2004). Reduction of NO_3^- and NO_2^- to NH_4^+ is accompanied by oxidation of dissolved sulphide (H_2S) to sulphate (SO_4^{2-}) via elemental sulphur as a reactive intermediate. DNRA performed by these and other sulphur bacteria is a globally widespread process (Jørgensen

---

* Corresponding author.
E-mail address: ssommer@geomar.de (S. Sommer).

http://dx.doi.org/10.1016/j.dsr.2016.03.001

and Nelson, 2004; and references therein). Massive occurrence of these organisms has not only been reported from the Peruvian and Chilean continental shelf (e.g. Gallardo, 1977; Gutiérrez et al., 2008, Mosch et al., 2012, this study), but also from OMZ sediments of the Arabian Sea (Jørgensen and Gallardo, 1999; Schmaljohann et al., 2001) the Benguela current ecosystem off Namibia (Gallardo et al., 1998) and hypoxic environments in the Baltic Sea (Dale et al., 2013; Noffke et al., 2016). Communities of *Thioploca* on the Californian margin have been suspected to enhance N loss by shunting, either actively or passively, part of their internal NO_3^- reservoir to closely associated anammox bacteria (Prokopenko et al., 2013).

Dense mat communities of sulphur oxidizing bacteria can significantly reduce the sulphide flux from the sediments to the overlying water column (Brüchert et al., 2003; Fossing et al., 1995; Teske, 2010; Teske and Nelson, 2006 and references therein; Zopfi et al., 2001). In organic carbon rich sediments with high rates of microbial sulphate reduction and underlying oxygen-depleted bottom waters, DNRA is an important sulphide detoxifying mechanism and gate-keeper between the benthic and pelagic sulphur and nitrogen cycles.

Members of the genus *Thioploca* very efficiently oxidize sulphide to levels near detection limit (Ferdelman et al., 1997; Thamdrup and Canfield, 1996; Bohlen et al., 2011). However, under sustained lack of bottom water oxygen (O_2), NO_3^- and NO_2^-, microbial sulphide production can overwhelm the sulphide oxidation capacity of the sulphur bacteria and lead to sulphide poisoning of life in the seabed (Gutiérrez et al., 2008). Sulphide-blackened dead *Thioploca* mats referred to as "*Thioploca nigra*" have been frequently observed on Chilean shelf sediments (Teske, 2010).

Here we report on the benthic N fluxes across the Peruvian margin under conditions of high sulphide release from the shelf sediments and bottom waters that were depleted in NO_3^- and NO_2^-. At the time of sampling, the benthic N cycle at the shallowest stations was strongly shifted to a non-steady state regime. However, an imbalanced benthic N cycle was a general feature found down to 400 m, although not as extreme as on the shelf. Consistent with previous reports, we find the shelf sediments acted as intense fixed N recycling sites, whereas sediments within the core of the OMZ and deeper tended to behave as fixed N sinks.

2. Methods

2.1. Description of study area

The eastern tropical south Pacific is characterized by one of the most pronounced oxygen minimum zones (OMZ) in today's ocean. It is maintained by the combination of sluggish ocean circulation and enhanced microbial subsurface respiration due to high primary production and associated export of organic matter at the continental margin (e.g., Wyrtki, 1962; Brandt et al., 2015). At the Peruvian margin, elevated productivity is caused by coastal upwelling (Strub et al., 1998) sustained by alongshore equatorward trade winds and cyclonic wind-stress curl, both varying in strength seasonally. Highest productivity is observed between 5° and 15°S (Echevin et al., 2008). Nutrient–rich but oxygen poor Equatorial Subsurface Water (ESSW) is supplied to the upwelling region by the Peruvian-Chile Undercurrent (PCUC) flowing poleward along the upper continental slope and the shelf between 50 and 300 m depth (Chaigneau et al., 2013). During its southward passage within the PCUC, the initially nitrate-rich ESSW becomes increasingly depleted in nitrogen, particularly within the bottom boundary layer (Kalvelage et al., 2013; Thomsen et al., 2015). Below the PCUC, observations revealed the existence of a weak equatorward flow, the Chile-Peru Deep Coastal Current (CPDCC) (Chaigneau et al., 2013; Pietri et al., 2014) carrying cold and low-saline Antarctic Intermediate Water (AAIW) northward.

During the measurement programme carried out on R/V Meteor cruise 92 from 6 January to 3 February 2013, moderate southeasterly winds prevailed along 12°S, typical for the austral summer season. Within about 55 km from the coast, ship-board measurements indicated average winds of 5 $m\ s^{-1}$ with sustained periods of winds below 1 $m\ s^{-1}$. In the first two weeks of January 2013, elevated poleward alongshore velocities above 0.25 $m\ s^{-1}$ were observed between 100 and 200 m depth associated with the PCUC, while the flow higher up on the shelf (<100 m) was weak (Thomsen et al., 2015). Towards the end of January, the PCUC separated from the continental slope forming a subsurface anticyclonic eddy in February. The evolution of the flow and the associated cross-slope exchange of solutes due to the presence of the eddy are detailed in Thomsen et al. (2015).

During the observational period, water masses along the continental margin at the thermocline level and below were low-oxygen ESSW and AAIW. Their presence led to a rapid decrease of O_2 levels with depth. Across the continental margin O_2 concentrations below the detection limit of the Winker titration (ca. 2 μM) were observed below ca. 30–50 m depth down to a water depth of ca. 500 m, at which point they gradually increased to about 50 μM at 1000 m (Fig. 1).

The biogeochemistry of the sediments and water column of the Peruvian margin was investigated along a latitudinal depth transect at 12°S from a water depth ranging from 74 m on the shelf to 989 m below the OMZ, equal to a horizontal distance of 80 km (Table 1, Fig. 1, Dale et al., 2015). Dissolved O_2 concentrations in the water column showed the presence of O_2-deficient water overlying the upper slope sediments, as described above.

Sediments on the upper continental slope and shelf off Peru between 11° and 15°S can be classified as fine grained, diatomaceous, organic carbon rich muds (>5 wt%) (Suess et al., 1987). Sediment accumulation rates on the shallow shelf down to 100 m at 12°S are very high (0.45 $cm\ yr^{-1}$) decreasing to <0.1 $cm\ yr^{-1}$ below 200 m (Dale et al., 2015). Organic carbon is preferentially preserved in the OMZ with burial efficiencies exceeding 70% (Dale et al., 2015). Sediments on the shelf and upper slope are covered with mats of the sulphide-oxidizing bacteria *Thioploca* and *Beggiatoa* (Levin et al., 2002; Mosch et al., 2012). Their biomass varies temporally depending on the redox potential of the overlying water column (Gutiérrez et al., 2008). At 12°S, mats completely covered the seafloor, with surface coverage decreasing down to 300 m (Dale et al., 2015). At the 409 m site, mats were absent and the surface 3 cm of sediments were instead characterized as foraminiferal ooze (Dale et al., 2015). Abundant nitrate-storing denitrifying foraminifera have been observed previously within the OMZ at 11°S and are suspected to play a major role in benthic N loss on the margin (Glock et al. 2013).

On the basis of bottom water O_2 distributions and sedimentary particulate organic carbon (POC) content, Dale et al. (2015) characterized the Peruvian margin at this latitude into 3 zones reflecting bottom water O_2 distributions and sedimentary POC content: (i) the shelf ($<$ ca. 200 m, POC 5–10%, $O_2 <$ detection limit (dl) at time of sampling) where non-steady state conditions are occasionally driven by periodic intrusion of oxygenated bottom waters (Levin et al., 2002; Gutiérrez et al., 2008), (ii) the core of the OMZ (ca. 200–500 m, POC 10–20%, $O_2 <$ dl) where periodic intrusions of oxic bottom waters are less likely, and (iii) the deep stations below the OMZ (POC $\leq$ ca. 5% and $O_2 >$ dl). We adopt the same notation in this work.