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Coastal hypoxia/anoxia as a source of CH$_4$ and N$_2$O

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Coastal hypoxia/anoxia as a source of CH$_4$ and N$_2$O

S. W. A. Naqvi et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Coastal
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S. W. A. Naqvi et al.

Full Screen / Esc

Abstract

We review here available information on distributions of methane (CH$_4$) and nitrous oxide (N$_2$O) from major, mostly coastal, oxygen (O$_2$)-deficient zones produced due to both natural processes and human activities (mainly eutrophication). Concentrations of both gases in subsurface waters are affected by ambient O$_2$ levels. In the case of CH$_4$, bottom-water O$_2$ content probably affects emission from sediments, believed to be the main source of water-column CH$_4$, as well as its oxidative loss in water itself. Highest CH$_4$ accumulation (several μM) occurs in silled basins having anoxic deep waters such as the Black Sea and the Cariaco Basin. One to two orders of magnitude smaller, but still significant, accumulation also occurs in bottom waters of open margins experiencing anoxia and in silled basins containing suboxic/severely hypoxic waters. In highly eutrophic waters over open continental shelves (such as the upwelling zone off Namibia and the "dead zone" in the Gulf of Mexico) high CH$_4$ concentrations (several hundred nM) may occur in non-sulphidic waters as well, but in these regions it is difficult to differentiate the hypoxia-induced enhancement from in situ production of CH$_4$ in the water column and, sometimes, large inputs of CH$_4$ associated with freshwater runoff or seepage from sediments. Despite the observed CH$_4$ build-up in low-O$_2$ bottom waters, methanotrophic activity severely restricts its emission from the ocean. As a result, an intensification or expansion of coastal hypoxic zones will probably not drastically change the present status where emission from the ocean as a whole forms an insignificant term in the atmospheric CH$_4$ budget. The situation is different for N$_2$O, the production of which is greatly enhanced in severely hypoxic waters, and although it is lost through denitrification in most suboxic and anoxic environments, the peripheries of such environments offer most suitable conditions for its production, with the exception of semi-enclosed/land-locked anoxic basins such as the Black Sea. Most O$_2$-deficient systems serve as strong net sources of N$_2$O to the atmosphere. This is especially true for regions of coastal upwelling with shallow oxygen minimum zones where a dramatic increase in N$_2$O production often occurs in rapidly denitrifying waters. Nitrous oxide

emissions from these zones are globally significant, and so their ongoing intensification and expansion is likely to lead to a significant increase in N_2O emission from the ocean. However, a meaningful quantitative prediction of this increase is not possible at present because of continuing uncertainties concerning the formative pathways to

5 N_2O as well as insufficient data from some key coastal regions.

1 Introduction

Methane (CH_4) and nitrous oxide (N_2O) are two important trace constituents of the atmosphere. Both CH_4 and N_2O are potent greenhouse gases that are approximately 300 and 25 times more effective, respectively, on a per molecule basis than carbon

10 dioxide (CO_2) in trapping infrared back radiation from the earth's surface. They also play important roles in atmospheric chemistry – CH_4 is the most abundant hydrocarbon in the atmosphere and N_2O is an important precursor for nitric oxide (NO) radicals which are involved in the destruction of ozone in the stratosphere. Both gases are produced by natural processes as well as by human activities. The latter include landfills,

15 livestock, fossil fuel exploitation, agriculture (rice paddies) and wastewater treatment for CH_4, and agriculture (application of N-fertilizers) and fossil fuel combustion for N_2O. As a result of anthropogenic emissions, average atmospheric concentrations of CH_4 and N_2O by 2007 had risen by 156% and 19% above the pre-industrial levels to 1789 and 321 parts per billion (ppb), respectively (Anonymous, 2008).

20 The ocean serves as a large source of N_2O to the atmosphere, accounting for at least one-third of all natural emissions (IPCC, 2007; Bange, 2006a). Although the ocean also emits CH_4 to the atmosphere, its contribution to the atmospheric CH_4 budget is minor (<2% – Reeburgh, 2007). Unlike the terrestrial sources, the impingement of human activities on oceanic emissions of these gases is not well understood and

25 poorly quantified. One important factor that exerts the key control on biological cycling of these gases in the ocean is the redox state of the environment, which is determined by the ambient oxygen (O_2) concentration. Containing carbon in its most reduced

Coastal hypoxia/anoxia as a source of CH_4 and N_2O

S. W. A. Naqvi et al.

(-4) form, CH_4 is produced in significant quantities only in anoxic environments. In the case of N_2O (which contains nitrogen in an intermediate oxidation state of $+1$), both oxidative (nitrification) and reductive (denitrification) production pathways exist. Denitrification [reduction of nitrate (NO_3^-) to elemental nitrogen (N_2) with N_2O as an
5 intermediate] is, of course, an anaerobic process. But even in nitrification [oxidation of ammonium (NH_4^+) to NO_3^- where N_2O is formed as a byproduct], the yield of N_2O relative to N_2 increases as the O_2 concentrations fall below about $0.5\,mL\,L^{-1}$ ($\sim 22\,\mu M$) (Goreau et al., 1980). Thus, changes in O_2 distribution will most likely alter source strengths of both CH_4 and N_2O. Such changes in subsurface O_2 field may be forced by
10 altered circulation/stratification in response to greenhouse warming, and/or by elevated respiration of organic matter produced as a result of enhanced nutrient supply from land.

The extent to which human activities are affecting/have affected physical processes that control subsurface O_2 distribution is unclear. It has been suggested that coastal
15 upwelling has become more vigorous since the 1940s due to an intensification of continental thermal lows adjacent to the eastern boundary upwelling regions off California, Northwest Africa, Iberian Peninsula and Peru (Bakun, 1990). More recently, the observed intensification of hypoxic conditions (see Table 1 for the terms used in this paper to define various stages of O_2 deficiency) in the California Current region has been
20 attributed to a change in water circulation over the shelf (Grantham et al., 2004; Bograd et al., 2008; Chan et al., 2008). Moreover, the observed and modelled decrease in O_2 concentrations in subsurface waters including the expansion of oceanic oxygen minimum zones (OMZs) point to physical causes such as decrease in surface concentration and slower subsurface ventilation (Joos et al., 2003; Stramma et al., 2008; Oschlies et
25 al., 2008; Shaffer et al., 2009). The growing deposition of anthropogenic nitrogen from the atmosphere that extends well beyond coastal waters (Galloway et al., 2004; Jickels, 2006; Duce et al., 2008) is also expected to contribute to the ongoing subsurface O_2 decline in the open ocean. According to Duce et al. (2008), atmospheric deposition of anthropogenic nitrogen could have led to an increase in oceanic N_2O emission by

Coastal hypoxia/anoxia as a source of CH$_4$ and N$_2$O

S. W. A. Naqvi et al.

$\sim 1.6\,\text{Tg N yr}^{-1}$ ($T=10^{12}$). While the exact mechanism of this increase is not known, some part of it might be due to enhanced production associated with O_2 depletion. In contrast with the atmospheric deposition, the riverine supply of reactive nitrogen that has been greatly altered by human activities (Seitzinger et al., 2002; Galloway et al., 2004) is largely confined to the coastal zone. Moreover, while the atmospheric deposition is mostly restricted to nitrogen, rivers also bring other macronutrients (phosphorus and silicon), of which phosphorus flux has also more than doubled as a result of human activities (Smith et al., 2003). The enhanced supply of (anthropogenic) nutrients (eutrophication) to coastal regions has led to development of hypoxia in many parts of the world (Diaz and Rosenberg, 2008, and references therein) that would, among other things, affect the production of CH_4 and N_2O. Here we review the information available on these gases from the coastal zones that are affected by natural as well as human-induced hypoxia/suboxia/anoxia.

2 Processes responsible for formation of O_2-depleted coastal systems

Oxygen depletion in seawater, as in all other aquatic systems, can occur due to natural processes as well as anthropogenic factors, and it is sometimes difficult to de-convolve the effects of these two forcings. For example, controversy persists concerning the cause(s) of hypoxia even for the best known of all coastal hypoxic systems – the "dead zone" of the Louisiana Shelf in the northern Gulf of Mexico (Rabalais et al., 2007; Swarzenski et al., 2008). All natural O_2-deficient aquatic environments have arguably been affected by human activities to varying degrees. Nonetheless, it is possible in most cases to identify the dominant driver of hypoxia. Thus, out of the systems being examined here (Fig. 1), hypoxia in the Gulf of Mexico, East China Sea and Tokyo Bay is largely human-induced, whereas in the remaining regions it is primarily of natural origin.

The most important oceanic O_2-deficient environments are formed naturally and have existed with varying intensities through geological times (Neretin, 2006). Today, a

number of semi-enclosed/land-locked seas and fjords experience anoxia due to stagnation of subsurface waters. The Black Sea, the Cariaco Basin and the central Baltic Sea are the best known of such water bodies. Of these, the first two are permanently anoxic below their sill depths whereas the third is periodically so. By contrast, in the

5   open ocean, severe O_2 depletion only occurs within the mesopelagic realm in a few well-demarcated geographical areas (Deuser, 1975). Such oxygen minimum zones (OMZs) can be easily identified in global maps of dissolved O_2 at depths of few hundred meters, an example of which (for 150 m, close to the upper boundary of OMZs) is shown in Fig. 1. The OMZs are located in the tropics and subtropics along the eastern

10   boundaries of the Atlantic and Pacific oceans. They develop because of a combination of slower water renewal, owing to the fact that these regions fall in the shadow of the subtropical gyres, and higher O_2 demand for respiration arising from high biological production in the overlying surface waters fuelled by nutrient enrichment through upwelling (Gruber, 2004). The OMZs in the Pacific (off western North America – Mexico,

15   and off western South America – Chile and Peru) are more voluminous than those in the Atlantic (off Southwest Africa – Namibia, and off Northwest Africa – Mauritania) because of the generally lower subsurface O_2 concentrations throughout the Pacific. In all but one (off Northwest Africa) of these four eastern-boundary upwelling systems (EBUSs), O_2 concentrations fall to suboxic levels. Due to its unusual geography – its

20   northward expanse is limited by the South Asian land mass at low latitudes - and resultant unique monsoonal circulation, the eastern boundary of the Indian Ocean does not experience vigorous upwelling and associated O_2 deficiency. Instead, the dominant variability in O_2 below the surface layer occurs in the north-south direction (Wyrtki, 1971). The OMZ is particularly intense (O_2<0.02 mL/L, ~1μM) and thick (lying be-

25   tween ~100/150 and 1200 m) in the Northwest Indian Ocean (Arabian Sea), which is the most productive part of the Indian Ocean because of nutrient enrichment of the euphotic zone through convective mixing in winter and upwelling in summer (Naqvi et al., 2003). Extension of the offshore OMZs to the coastal region occurs through the process of upwelling. Thus, advection of low-O_2 waters is prerequisite to (natural)

development of coastal hypoxia. However, in addition to the initial O_2 content of the upwelling water, the intensity of O_2 deficiency over the shelf is modulated by a number of factors – local circulation/hydrography especially stratification, upwelling intensity, shelf width, and primary production – that determine the balance between oxygen con-
5 sumption and supply in subsurface waters.

Coastal hypoxic zones produced due to anthropogenic activities, whose number is steadily increasing over the past few decades (Diaz and Rosenberg, 2008), are mostly located in nearshore waters and estuaries in areas that are subject to high loading of nutrients and/or organic matter from terrestrial sources. Most of this loading occurs
10 through river runoff, although in the case of nitrogen atmospheric inputs are also important (Duce et al., 2008). This in conjunction with stratification caused by freshwater additions makes the estuaries and coastal zones off major rivers especially susceptible to deoxygenation. The continental shelf off the Mississippi River mouth in the Gulf of Mexico, the Chesapeake Bay that receives outflows from a number of rivers such as the
15 Susquehanna and the Potomac, and the coastal region off the Changjiang in the East China Sea (ECS) are the best examples of such systems. Hypoxia in these systems generally exhibits large seasonality due to changes in river runoff and solar insolation, and is generally at its maximum intensity in summer (e.g. Rabalais and Turner, 2006).

3 Brief overview of CH_4 and N_2O cycling in the ocean

20 ### 3.1 Methane

The oceanic CH_4 biogeochemistry has recently been reviewed by Reeburgh (2007). Its concentrations in the open-ocean water column are generally quite low (a few nM). Large CH_4 build-up does not occur even in the open-ocean suboxic zones because methanogenesis, the final step in the decomposition of organic matter using CO_2, is
25 inhibited by the presence of other electron acceptors (oxygen, oxidized nitrogen, manganese and iron species, and sulphate). Conditions favouring methanogenesis usually

Coastal hypoxia/anoxia as a source of CH_4 and N_2O

S. W. A. Naqvi et al.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

develop in sediments where below a certain horizon (the sulphate-CH_4 transition) sulphate is almost totally depleted. Despite the high (mM) CH_4 concentrations below the sulphate-CH_4 interface, the very low levels in the water column – the deep water is typically undersaturated with respect to the atmosphere – point to efficient oxidation, both in the sediment and water column (Rehder et al., 1999; Reeburgh, 2007).

The upper ocean is characterized by relative higher CH_4 concentrations – close to saturation at the seasurface with a maximum located near the base of the mixed layer. The cause of the ubiquitous occurrence of the maximum in well-oxygenated water – the so-called oceanic CH_4 paradox – has long been debated. Several explanations for the subsurface methane maximum have been offered and include both in situ production and advective transport of methane produced elsewhere. For example, it has been speculated that production with anoxic environments, most probably within guts of zooplankton, accounts for the maximum (Oremland, 1979; Reeburgh, 2007, and references therein). Coastal waters may also contain elevated CH_4 concentrations due to supply from coastal marshlands/estuaries (Scranton and McShane, 1991; Bange et al., 1994; Jayakumar et al., 2001; Bange 2006b) and from sediments, particularly in areas of hydrocarbon seepage or hydrate destabilization, resulting in pronounced subsurface maxima extending offshore from the continental margin that are distinct from the mixed layer maximum mentioned above (e.g. Scranton and Brewer, 1977; Brooks et al., 1981; Cynar and Yayanos, 1991; Ward, 1992; Tilbrook and Karl, 1995). More recently, it has been shown that CH_4 may be produced aerobically through decomposition of methylphosphonate that may serve as a source of phosphorus in phosphate-poor environments such as tropical surface waters (Karl et al., 2008). To date, however, the paradox remains unresolved.

3.2 Nitrous oxide

Bange (2008) has provided a comprehensive review of oceanic biogeochemistry of N_2O. Surface waters of the ocean are generally slightly supersaturated with respect to the atmospheric N_2O (~104%; Nevison et al., 1995), but much higher supersaturation

Coastal hypoxia/anoxia as a source of CH_4 and N_2O

S. W. A. Naqvi et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄ | ►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

occurs in regions that experience coastal upwelling and are affected by O_2-deficency in subsurface waters (e.g. Bange et al., 2001a; Nevison et al., 2004). An important aspect of N_2O distribution in the ocean is the inverse relationship with O_2; this feature, recognized by early workers, prompted the suggestion that nitrification was the domi-
5 nant process responsible for N_2O production (Yoshinari, 1976). Subsequently several authors reported linear relationships between ΔN_2O ($= N_2O_{observed} - N_2O_{saturation}$) and apparent oxygen utilization ($AOU = O_{2saturation} - O_{2observed}$) from various oceanic areas (e.g. Elkins et al., 1978; Oudot et al., 1990; Naqvi and Noronha, 1991; Naqvi et al., 1994). This relationship holds as long as the O_2 concentration does not fall below
10 $\sim 0.5\,\text{mL}\,\text{L}^{-1}$ after which a sharp non-linear N_2O build-up occurs as O_2 is further consumed (Codispoti and Christensen, 1985; Codispoti et al., 1992). Once the system turns suboxic, however, a depletion of N_2O takes place to levels below saturation, a trend consistently seen in all major open-ocean suboxic zones (Elkins et al., 1978; Cohen and Gordon, 1978; Naqvi and Noronha, 1991; Farias et al., 2009a). The sen-
15 sitivity of N_2O production and consumption to minor changes in O_2 in the low range has led to a large number of studies focussing on N_2O distribution in the OMZs (Elkins et al., 1978; Cohen and Gordon, 1978; Codispoti and Christensen, 1985; Codispoti et al., 1992; Law and Owens, 1990; Naqvi and Noronha, 1991; Upstill-Goddard et al., 1999; Bange et al., 2001b; Castro-Gonzalez and Farias, 2004; Farias and Cornejo,
20 2007; Cornejo et al., 2007; Farias et al., 2009a). The low N_2O concentrations within the nitrite (NO_2^-)-bearing waters are widely believed to arise from its utilization as an electron acceptor by heterotrophic bacteria (which convert it to N_2). Despite the existence of a sink for N_2O within the secondary nitrite maximum of the open-ocean OMZs, these zones still serve as disproportionately large net sources of N_2O because of high
25 N_2O concentration at their peripheries. The mechanisms responsible for this accumulation still continue to be poorly understood. Based on the isotopic evidence, Dore et al. (1998) suggested that the shallow N_2O maximum in the North Pacific is formed largely through nitrification, whereas Naqvi et al. (1998) proposed that a coupling between nitrification and denitrification could be a more important formative pathway for

Coastal hypoxia/anoxia as a source of CH_4 and N_2O

S. W. A. Naqvi et al.

S. W. A. Naqvi et al.

the upper N$_2$O maximum in the Arabian Sea. Nicholls et al. (2006) demonstrated that this N$_2$O maximum is produced largely through the reduction of NO$_2^-$ to N$_2$O, but whether this reduction is carried out by denitrifiers or nitrifiers still needs to be resolved (see also Shailaja et al., 2006). As we will see in the following section the pattern of variability observed in the coastal suboxic zones sometimes deviates from the trend observed in the open-ocean OMZs.

4 Methane and nitrous oxide in coastal hypoxic zones

4.1 Eastern Atlantic Ocean

4.1.1 Off Northwest Africa

The region off Northwest Africa (Morocco-Mauritania) in the eastern equatorial Atlantic Ocean (the Canary Current System) is one of the four major EBUEs. It is also the only one where subsurface O$_2$ depletion does not qualify to be classified as hypoxic, because of the relatively high initial O$_2$ content of waters upwelling over the shelf. However, given the ongoing deoxygenation of subsurface waters in the North Atlantic, there are concerns that hypoxia in subsurface waters may develop in future in this region as well (Stramma et al., 2008).

There are at present no published data on N$_2$O from this area. However, Kock et al. (2008) carried our extensive measurements of CH$_4$ in atmospheric and surface seawater samples collected off Mauritania during two cruises conducted in March/April 2005 and February 2007. They found saturations reaching up to 200% in the up-welled water. The annual CH$_4$ emission from the region was quantified as 1.6–2.9 Gg CH$_4$(G=10^9), which is not very significant in comparison to global supply to the atmosphere.

4.1.2 Off Southwest Africa

The upwelling zone off Southwest Africa (Namibia) supports the highest primary production rates of all the four major EBUEs (Carr, 2002). This, however, does not translate into a proportionately high fish yield because of intense respiration of organic matter in the water column and shelf sediments that culminates in the prevalence of sulphidic conditions in bottom waters (Chapman and Shannon, 1985; Brüchert et al., 2006; van der Plas et al., 2007; Lavik et al., 2009). These conditions are apparently not suitable for fisheries. In addition to respiration of locally-produced organic matter, the intensity of O_2 deficiency is also modulated by the initial O_2 content of upwelling waters. There are two main upwelling centres in this region located off Cape Frio in the north and Luderitz in the south. Upwelling at these locations is fed by intermediate waters with very different O_2 contents: the hypoxic Angola Basin Central Water off Cape Frio and more oxygenated Cape Basin South Atlantic Central Water off Luderitz, with the boundary between the two subsurface water types located around 25° S latitude (Monteiro et al., 2008). Once over the shelf, these waters move northward (from Luderitz) or southward (from Cape Frio) and it is the relative contribution from these sources that controls the variability of O_2 deficiency at any given site on seasonal as well as inter-annual time scales (Monteiro et al., 2006, 2008).

The region is important for redox nitrogen transformations (Kuypers et al., 2005; Lavik et al., 2009). Surprisingly, however, to our knowledge there have not been any measurements of N_2O in the water column in this area. On the other hand, CH_4 biogeochemistry in the region has attracted considerable attention largely due to "gas eruptions" (presumably a mixture of CH_4 and H_2S) that usually occur in the late summer (Weeks et al., 2002; Emeis et al., 2004; Brüchert et al., 2006). These eruptions are large enough to be seen by a satellite (Weeks et al., 2002) and the sediment mobilization they cause can occasionally give birth to ephemeral mud islands (Copenhagen, 1953). Several sedimentary profiles of CH_4 have been published from the region (Emeis et al., 2004; Brüchert et al., 2006). High primary production leads to

an accumulation of organic carbon and consequently high (anaerobic) respiration in sediments (Brüchert et al., 2006, and references therein). Bacterial reduction of sulphate coupled to degradation of organic matter is intense in the sediment, especially in the upper 10 cm. Sulphate gets fully consumed and methanogenesis occurs at rela-
5 tively shallow depths (tens of centimeters to a few meters). Accordingly, H_2S and CH_4 accumulate in porewaters in high concentrations (to ~22 and 8 mM – Brüchert et al., 2006). Therefore, the source of both gases in the overlying water column in all likelihood is sedimentary even though the relative importance of eruptions and diffusion in supplying these gases to the overlying water column is not quite clear. Emeis at
10 al. (2004) suggested that the gases might be released from unconsolidated sediments following physical changes in the sediment or in the overlying water column or even pressure changes arising from rainfall over land that could be transmitted to the sediment through fossil river beds. Obviously such inputs are episodic and even in their absence the water-column build-up of H_2S can be explained by diffusive fluxes alone
15 (Brüchert et al., 2006, Lavik et al., 2009). This probably applies to CH_4 as well.

To our knowledge, there is only one published report available so far from the region dealing with water column distribution of CH_4 based on chemical analysis (Scranton and Farrington, 1977). Their observations off Walvis Bay revealed some exceedingly high values (reaching up to 879 nM) both close to the surface and in near bottom-
20 waters, which were sulphidic over the inner shelf despite little upwelling occurring during the period of the observations (late December 1975–early January 1976). At mid-depth, lower CH_4 concentrations (forming a minimum) probably resulted from the advection of offshore water. The high concentrations in near-surface waters could arise from inputs from sediments at very shallow depths followed by lateral mixing/offshore
25 advection of CH_4-rich waters. However, Scranton and Farrington opined that some in situ production of CH_4 was probably also occurring in the upper water column.

Results of a high-resolution (hourly) time series, obtained with a mooring having O_2 and CH_4 sensors at 85 m depth, deployed for one year in the same area reveal a tight covariance between the two gases (Monteiro et al., 2006). Methane could not be de-

tected until the O_2 content had declined to $0.2\,\mathrm{mL\,L^{-1}}$ in early March 2003 (Fig. 2). The concentrations remained elevated for an extended period thereafter (from May to August), but with brief interruptions associated with increases in the O_2 concentration. The seasonal-scale CH_4 enrichment in bottom waters is modulated by event-scale ad-
5 vection of water as well as by daily-time-scale fluxes of O_2. Monteiro et al. (2006) proposed that anoxia off Namibia is initially triggered by the advection of equatorial hypoxic waters and then sustained by the respiration of locally produced organic mat-ter. The remarkable inverse relation between O_2 and CH_4 reflects the importance of bottom-water O_2 levels in controlling CH_4 efflux from the sediment probably through
10 controls on its production and consumption (oxidation).

4.2 Northern Indian Ocean

The northern Indian Ocean comprises two major basins, the Arabian Sea in the north-west and the Bay of Bengal in the northeast. These basins experience very different hydrographic and climatic conditions. The Arabian Sea is a region of negative water
15 balance where evaporation far exceeds precipitation and runoff while the reverse holds true for the Bay of Bengal. Moreover, the Southwest Monsoon winds are also stronger over the Arabian Sea, forcing upwelling along both the western (off Somalia, Yeman and Oman) and eastern (off India) boundaries (Naqvi et al., 2006a). Both basins ex-perience severe oxygen depletion at mid-depths. In fact, the minimum Winkler O_2
20 concentrations in the two basins do not differ by more than $0.05\,\mathrm{mL\,L^{-1}}$ ($\sim2\,\mu M$), and yet a secondary nitrite maximum is not observed in the Bay of Bengal and NO_3^- con-centration at the core of the OMZ is higher by a factor of ~2 in the Bay of Bengal as compared to the Arabian Sea (Naqvi et al., 2006a). The vertical extent of the OMZ is smaller in the Bay of Bengal than in the Arabian Sea (where it is the thickest found any-
25 where in the ocean with $O_2<0.1\,\mathrm{mL\,L^{-1}}$ prevailing from 100–150 m to 1000–1200 m). Because of the high coastline-to-ocean area ratio and the wide depth range over which the O_2 deficiency extends, the OMZs of the northern Indian Ocean impinge upon a very

large area of the continental margin: as much as two-thirds of the global continental margin area in contact with bottom waters having $O_2 < 0.2\,\mathrm{mL\,L^{-1}}$ is found here (Helly and Levin, 2004).

Despite the enormous river runoff into the Bay of Bengal/Andaman Sea and huge consumption of synthetic fertilizers in South Asia, the total flux of dissolved inorganic nitrogen by rivers to the Bay of Bengal is relatively modest ($<0.5\,\mathrm{Tg\,N\,yr^{-1}}$ – Naqvi et al., 2009a). This is one reason why hypoxic conditions are not known to develop over the inner shelf off the mouths/deltas of major rivers (e.g. Ganges/Brahmaputra and Irrawaddy) unlike, for example, the Gulf of Mexico; the other is that upwelling is very weak and the upwelled water does not reach sufficiently close to the coast. By contrast, O_2-depleted waters ascend to very shallow depths both along the western and eastern boundaries of the Arabian Sea (Naqvi et al., 2006a). There are, however, four important differences between the western and eastern boundary upwelling environments in the Arabian Sea: (1) upwelling is far more vigorous in the west, which is, in fact, the only major western-boundary upwelling system in the world. Driven by strong southwesterly winds, the strong Ekman flow quickly transports upwelled water offshore to a distance exceeding 1000 km (Naqvi et al., 2006a). (2) The water upwelling in the western Arabian Sea is derived from the south and has relatively high initial O_2 concentration. (3) Unlike the eastern Arabian Sea, there is no freshwater runoff and the upper layer is very weakly stratified in the western Arabian Sea. (4) The continental shelf in the western Arabian Sea is generally narrow which together with vigorous upwelling keeps the residence time of upwelled water over the shelf quite short. The western Arabian Sea, therefore, does not experience the kind of O_2 depletion (suboxic and anoxic conditions in the water column) that distinguishes the western continental shelf of India.

During the Southwest Monsoon the eastern Arabian Sea behaves like a mini EBUE with equatorward surface flow (as against the poleward flow during the Northeast Monsoon), a poleward undercurrent, and upwelling that is both locally and remotely forced (as against downwelling during the Northeast Monsoon) (Naqvi et al., 2006b, c). How-

ever, a thin (<10 m) freshwater lens, formed as a consequence of intense rainfall over the coastal zone, usually prevents the upwelled water from surfacing. The upwelled water is drawn from the undercurrent just off the shelf break that has O_2 content marginally above suboxia. Thus, the combination of sluggish upwelling, low initial O_2 content of the upwelled water, wide shelf, and very strong thermohaline stratification at very shallow depths leads to the formation of the largest natural hypoxic zone (area $\sim$200 000 km^2) in the coastal zone anywhere in the world (Naqvi et al., 2000). It is thus best suited to investigate the effect of coastal hypoxia on cycling of CH_4 and N_2O.

4.2.1 Methane

High saturations of CH_4 (124–286%) in waters upwelled to the surface in the western Arabian Sea have been observed by a number of investigators (Owens et al., 1991; Bange et al., 1998; Upstill-Goddard et al., 1999) These studies focused only on CH_4 distribution at the sea surface. Therefore, even though the bottom waters over the Omani shelf may sometime become hypoxic during the late Southwest Monsoon (S. W. A. Naqvi, unpublished data), the contribution of hypoxia in maintaining the observed high surface CH_4 concentrations cannot be evaluated. However, as elevated CH_4 concentrations also occur in upwelled waters outside the hypoxic zones (e.g. off Mauritania – Kock et al., 2008), at least a part of CH_4 is expected to be produced in the water column (Owens et al., 1991). It may also be noted that surface waters in the Arabian Sea are always phosphate-replete because of large-scale pelagic denitrification in the region (Naqvi, 1987; Morrison et al., 1998). Yet, the upper layer CH_4 maximum is prominently found in the region (Owens et al, 1991), and so its formative mechanism should be different from that proposed by Karl et al. (2008).

Jayakumar et al. (2001) measured CH_4 along a number of coast-perpendicular transects off the central and southwest coast of India during the Southwest Monsoon of 1997 to add to measurements made along a longer transect off Goa during the Spring Intermonsoon of the previous year. Figure 3 shows a typical cross-shelf CH_4 section along with corresponding sections of temperature, salinity, oxygen and nutrients off

Coastal hypoxia/anoxia as a source of CH_4 and N_2O

S. W. A. Naqvi et al.

Goa for the Southwest Monsoon. These sections provide examples of the aforementioned occurrence of strong thermohaline stratification (Fig. 3a, b) and the development of extreme O_2 deficiency within a few meters of the sea-surface (Fig. 3c).

The most striking feature of CH_4 distribution (Fig. 3e) is the sharp onshore–offshore gradient with the concentrations decreasing offshore at all depths. Measurements during the Spring Intermonsoon yielded relatively lower and spatially more uniform (3.5–5.5 nM) concentrations (Jayakumar et al., 2001). Higher concentrations during the Southwest Monsoon can arise from two different sources – transport from coastal wetlands and diffusion from underlying sediments. The former source is predominant over the inner shelf as evident from the association of peak CH_4 values (reaching up to 48 nM, corresponding to over 2500% saturation) with the low-salinity cap (Fig. 4). Even higher methane levels (up to 248 nM, ∼13 000% saturation at ∼15 salinity) were recorded within the Mandovi Estuary (Jayakumar et al., 2001). While in case of the shallow section (over the inner shelf), highest concentrations occur at the surface, the concentrations remain elevated even below the pycnocline, which in part may be due to some vertical mixing. By contrast, further offshore (over the mid- and outer shelf), the concentration maximum occurs close to the seafloor, indicating CH_4 emission from the sediment to the overlying water column. Nevertheless, the observed concentrations are not anomalously high (generally <10 nM) and are comparable to maximal CH_4 concentrations in the upper water column of the open Arabian Sea (Owens et al., 1991; Jayakumar et al., 2001). However, the conditions change once the bottom waters become sulphate reducing. This happens after nitrate gets fully consumed through denitrification/anaerobic ammonium oxidation (anammox) over the inner- and mid-shelf regions usually by late August/early September (Naqvi et al., 2006b, c). Methane levels at that time increase substantially to 40–50 nM in sulphidic bottom waters (Gayatree Narvenkar, unpublished data).

The source of CH_4 diffusing from shallow sediment is most likely to be from contemporaneous biogenic production although methane from deeper reservoirs (either petrogenic or biogenic) can also form seeps or plumes. There are reports of gas-charged

sediments a few metres below the seafloor off the western coast of India, inferred from acoustic masking. The total amount of CH_4 trapped in such sediments over the inner continental shelf has been estimated as 2.6 Tg (Karisiddaiah and Veerayya, 1994). However, diffusion from this source alone does not appear to be sufficient to sustain the observed CH_4 supersaturation in the overlying waters (Jayakumar et al., 2001).

There are few data on CH_4 distribution in the sediment off the coast of India, but the sulphate- CH_4 transition does not appear to be located very close to the surface. Measurements of sedimentary sulphate reduction rates over the inner shelf off Goa yielded surprisingly low values (generally <10 nmol cm^{-3} d^{-1}). Moreover, porewater sulphide concentrations are also quite low (few μM) while sulphate concentrations do not exhibit any significant decrease with depth in the upper 20–30 cm for which data are available (S. W. A. Naqvi and V. Brüchert, unpublished data). Thus, conditions favouring methanogesis do not seem to exist in the upper few tens of centimeters in the sediments. However increased hypoxia in this area, with accompanying increases in carbon flux and lower oxygen, would likely increase the importance of sulphate reduction and methane production within the sediments.

Given the large geographical changes in surface saturation and wind speed, the computed fluxes of CH_4 from the Arabian Sea vary greatly [form near 0 to 64 μmol m^{-2} d^{-1} – see Naqvi et al. (2005) for a review]. The highest emissions are observed during the Southwest Monsoon from waters upwelling in the western Arabian Sea (up to 13.9 μmol m^{-2} d^{-1} – Owen et al., 1991) and from the inner shelf in the eastern Arabian Sea that is affected by land runoff (up to 64 μmol m^{-2} d^{-1} – Jayakumar et al., 2001). Despite these high fluxes, the highest estimate of CH_4 emission from the Arabian Sea as a whole is only 0.1–0.2 Tg yr^{-1}, which is merely 0.4–0.7% of the total oceanic source and is therefore not very significant (Naqvi et al., 2005).

Methane measurements along three transects over the shelf off Bangladesh in January 1994 by Berner et al. (2003) yielded above-saturation surface concentrations, ranging between 3.17 and 38.3 nM and driving a sea-to-air flux of 0.22–24.9 μmol m^{-2} d^{-1}. The highest values were observed off the mouth of Ganges/Brahmaputra, re-

flecting inputs by river water. This is consistent with high CH_4 concentrations of 10.3–59.3 nM reported by Biswas et al. (2003) from the Hooghly Estuary (a distributory of the Ganges). Berner et al. (2003) found hypoxic water ($O_2 < 0.5$ mL L^{-1}) over the seafloor at depths >60–70 m. Methane concentration in this water reached up to 12.9 nM, so it appears that some enhancement of CH_4 from the sediment underlying hypoxic waters could be occurring over this segment of the shelf. The observed CH_4 concentrations are lower than observed in other regions of river runoff (e.g. in the Gulf of Mexico, see below), in spite of Ganges/Brahmaputra delta containing one of the most extensive mangrove swamps in the world (the Sundarbans), but then the observations were not made during periods of highest river runoff.

4.2.2 Nitrous oxide

High N_2O saturations in the Arabian Sea surface waters, averaging 167–186%, were first noticed by Law and Owens (1990) and Naqvi and Noronha (1991). Subsequent studies have led to a large data base on N_2O distribution in the region that also includes coastal waters off Somalia, Oman and India. An early synthesis of surface measurements by Bange et al. (2001a) shows that the highest concentrations and sea-to-air fluxes occur in the upwelling zones off Oman and India during the Southwest Monsoon. In the western Arabian Sea, surface saturations averaging 230±46% off Oman (in 1994) and up to 330% off Somalia (in 1992) were recorded by Bange et al. (1996), and de Wilde and Helder (1997), respectively. These high values directly arise from the high concentration of N_2O in the upwelling water, which is not suboxic off Oman (Naqvi, 1991) and contains high dissolved N_2O (Bange et al., 2001b). Observations at 12 stations located over the Omani shelf during September 2004 (Gayatree Navenkar, unpublished data) yielded surface N_2O concentrations ranging from 9.7 to 24.7 nM (156–358% saturation), consistent with previous data. However, depth profiles of N_2O at these stations did not show any anomalously high values, with the maximal subsurface concentration being 48.8 nM. Only at one station was there an indication of mild denitrification occurring in the bottom water with a consequent decrease in N_2O.

The western continental shelf of India is one of the most interesting and important oceanic sites for N_2O cycling; arguably it is also the best studied. Distribution of N_2O over various segments of the coast using data collected on a number of cruises has been investigated (Naqvi et al., 1998, 2000, including supplementary data therein;
Naqvi et al., 2006a, b, c, 2009b). In addition, measurements of N_2O have also been made since 1997 during monthly/fortnightly trips to a coastal quasi-time series station (the Candolim Time Series – CaTS) located off Goa (Lat. $15°31'$ N, Long. $73°39'$ E) at a water depth of ~ 26 m. The monthly/fortnightly-averaged records showing annual cycles of key oceanographic parameters are shown in Fig. 5.

During the Northeast Monsoon and Spring Intermonsoon periods, when the water column over the Indian shelf is well oxygenated (also see Fig. 6a), the water is moderately supersaturated with atmospheric N_2O. Nitrous oxide begins to accumulate as O_2 is consumed in the subsurface layer after the onset of upwelling in May. The concentrations continue to rise even after the system becomes suboxic. In fact, the greatest build-up of N_2O coincides with the rapid decline in NO_3^- and accumulation of NO_2^-, pointing to N_2O production through denitrification. This is in sharp contrast with the pattern observed in open ocean OMZs, where, as mentioned above, the secondary nitrite maximum is invariably characterized by a minimum in N_2O. However, the concentrations decrease rapidly once the environment becomes sulphate reducing, which indicates that the observed high concentrations cannot be due to inhibition of N_2O reductase activity by H_2S (Senga et al., 2006). This temporal trend, which has been repeatedly observed at the CaTS site, is consistent with the spatial variability along cross-shelf sections, an example of which is provided in Fig. 6b. As the water ascends over the shelf, it quickly loses whatever little O_2 it initially contained, leading to the prevalence of hypoxic conditions over the inner shelf, suboxic conditions (denitrification) over the mid-shelf and anoxic conditions (sulphate reduction) over the inner shelf. The highest concentrations of N_2O – the record measurement is 765 nM – are found over the suboxic mid-shelf and in mid-water over the inner shelf. In addition to the association of high N_2O and NO_2^- (up to 16 μM) values, accumulation of N_2O during

denitrification has also been demonstrated by Naqvi et al. (2000) through incubation in air-tight bags of water samples that were initially not suboxic. It was suggested by these authors that frequent aeration of the water through turbulence could suppress the activity of N_2O reductase allowing transient production of N_2O. In regions where, and during periods when, subsurface O_2-deficiency is not severe enough to allow for the onset of suboxic conditions, as happens off the southwest coast of India (generally south of ~12° N latitude), high N_2O concentrations (>100 nM) have not been recorded (Naqvi et al., 2006a).

Maximal surface concentration observed over the Indian shelf, which is also the highest reported from the oceanic surface waters, is 436 nM (corresponding to 8250% saturation), with the average exceeding 37 nM (Naqvi et al., 2006b). The highest computed flux is 3243 μmol m^{-2} d^{-1}, with the average ranging from 39 to 264 μmol m^{-2} d^{-1} depending upon the model of air-sea exchange chosen and the wind speed (5–10 m s^{-1} – Naqvi et al., 2006b). The total emission of N_2O from the Indian shelf is thus computed to be 0.05–0.38 Tg N_2O for the upwelling season. For comparison, the total annual efflux of N_2O from the Arabian Sea as a whole (that did not take into account the abnormally high values from the Indian coast) was estimated to range between 0.33 and 0.70 Tg by Bange et al. (2001a). It has been suggested that the natural low-O_2 system off India has intensified in recent years most likely because of enhanced nitrogen loading through runoff and atmospheric deposition (Naqvi et al., 2000, 2006b, 2009b). Because N_2O data from this region go back only to 1997, it is not clear to what extent has this intensification affected N_2O cycling. However, given the observation that the highest N_2O concentration is observed with the most intense O_2 deficiency, we speculate that an increase in production is likely to have occurred relative to the pristine conditions.

Unlike the Arabian Sea, the OMZ of the Bay of Bengal is just short of being suboxic in that a secondary nitrite maximum generally does not occur in the region. Consequently, vertical profiles of N_2O show a single broad maximum within the OMZ (Naqvi et al., 1994). Surface saturations and atmospheric fluxes from the region are, therefore, much

lower. Also, although some upwelling does occur along the Indian east coast during the Southwest Monsoon, the shelf is narrow and the low-salinity layer formed as a result of enormous freshwater inputs to the Bay of Bengal through rainfall and river runoff is several tens of meters thick meaning that the upwelled water does not reach very shallow depths (Naqvi et al., 2006a). Accordingly, N_2O concentrations over the shelf do not exceed a few tens of nM (Naqvi et al., 1994, 2006a).

4.3 Eastern North Pacific Ocean

The eastern tropical/subtropical North Pacific experiences conditions that are typical of an oceanic eastern boundary: the surface current (the California Current) flows equatorward while northwesterly winds drive intense upwelling along the west coast of the United States and the northwest coast of Mexico. An extensive OMZ with $O_2 < 0.2\,\text{mL L}^{-1}$ ($9\,\mu M$) extends ~1500 km offshore from the Mexican coast (Deuser, 1975). The suboxic zone, confined to the tropical region, is among the best investigated for redox nitrogen cycling (Cline and Richards, 1972; Cline and Kaplan, 1975; Ward et al., 2008). Low-O_2 concentrations also extend at mid-depths quite far north off the west coast of United States (especially in the silled basins of the Southern California Bight), although the water column does not seem to be reducing (e.g. Sigman et al., 2003). As already mentioned, large decreases in subsurface O_2 concentrations in the California Current System have been recorded recently. These are believed to result from advection of O_2 depleted water over the shelf (Grantham et al., 2004; Bograd et al., 2008; Chan et al., 2008).

4.3.1 Methane

The open-ocean suboxic zone of the eastern tropical North Pacific (ETNP) contains the largest pool of CH_4 in the open ocean (Sansone et al., 2001). Vertical CH_4 profiles obtained by Burke et al. (1983) at several stations located parallel to but away from the Mexican coast, showed a ubiquitous shallow (50–150 m) CH_4 maximum outside the

Coastal hypoxia/anoxia as a source of CH_4 and N_2O

S. W. A. Naqvi et al.

zone of suboxia with concentrations reaching up to 6.5 nM. This maximum extended much deeper (to at least 400 m, which was the maximum depth of sampling) at stations that were located within the suboxic zone. This was attributed to in-situ production of CH_4 through microbial activity associated with suspended particles recycled by zoo-
5 plankton grazing. It may be a noted that a secondary particle (turbidity) maximum was found within suboxic waters. A similar pattern – elevated CH_4 levels in suboxic waters associated with a turbidity maximum – was also observed in the Arabian Sea by Jayakumar et al. (2001). A subsequent study by Sansone et al. (2001) in the ETNP along a transect extending offshore from the Mexican coast also found relatively higher
10 CH_4 concentrations in suboxic waters. Methane levels were particularly elevated (28 nM at 350 m) at the station located closest to the coast. These authors also measured the carbon isotopic composition of CH_4 and concluded that while CH_4 in the upper half of the pool was being produced in situ during decomposition of sinking organic matter, that in the lower half of the pool was derived from the continental margin. In a more
15 recent study, Sansone et al. (2004) focused on CH_4 cycling along the western Mexican continental margin in and around the Gulf of California. Their sampling stations were positioned both in the coastal basins and over the open margins. Those stations where water depth exceeded the lower boundary of the OMZ had lower CH_4 concentrations than the station where the OMZ impinged upon the seafloor, consistent with
20 higher CH_4 supply to and/or lower oxidative loss within the OMZ. The highest build-up of CH_4 (up to 78 nM) was found to occur in bottom waters of silled basins, presumably through diffusion from the seafloor. Apparently this did not affect CH_4 distribution outside the basins, perhaps because of water column CH_4 oxidation. Diffusive fluxes from the sediment (0.24–5.5 μmol m^{-2} d^{-1}) computed from porewater CH_4 gradients were
25 similar to the sea-to-air fluxes (0.5–5.9 μmol m^{-2} d^{-1}), and since oxidative loss must be occurring in the water column, a source of CH_4 in the water column is also required to sustain the sea-to-air flux.

Several studies have been conducted on CH_4 cycling in coastal waters further north in the California Current System (e.g. Ward, 1992; Cynar and Yayanos, 1992; Tilbrook

Coastal hypoxia/anoxia as a source of CH$_4$ and N$_2$O

S. W. A. Naqvi et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

◄ | ►◄

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

and Karl, 1995; Kessler et al, 2008). The usual trend of CH_4 supersaturation in surface waters with a subsurface maximum has been reported but no major anomalies have been seen that could be attributed to hypoxia. There seems to be general agreement that inputs from the continental margin are important in maintaining water column

5   CH_4 maxima, particularly because there is extensive hydrocarbon seepage in the region. For example, Cynar and Yayanos (1992) observed values as high as 1416 nM between Point Conception and Santa Barbara, which could only be produced by CH_4 emission from hydrocarbon seeps. Radiocarbon measurements confirmed the importance of seep-derived CH_4 in the Santa Barbara Basin (Kessler et al., 2008). Due to

10   high CH_4 concentration in subsurface waters, upwelling enhances supersaturation in surface waters (Rehder et al., 2002).

4.3.2   Nitrous oxide

Nitrous oxide cycling in open ocean OMZ of the ETNP has been well known since the pioneering work of Cohen and Gordon (1978) that revealed the existence of dou-

15   ble maxima in vertical N_2O profiles in the region affected by pelagic denitrification. This was attributed to consumption of N_2O by denitrifiers within the secondary nitrite maximum and its production at the boundaries by nitrifiers, a view largely supported by subsequent measurements including dual isotopic composition of N_2O (Yoshinari et al., 1997; Yamagishi et al., 2007). Yamagishi et al. (2007) presented data from two stations

20   – one each located within the heart of the suboxic zone of the ETNP and the central Gulf of California – on N_2O concentration and its isotopic composition. The latter also included isotopomeric analysis (i.e. the location of ^{15}N in linear N_2O molecule) which provides information on the mechanisms of N_2O production. In the ETNP, the highest N_2O concentration ($\sim$87 nM) and the lowest isotopic values (e.g. $\delta^{15}N^{bulk}$=3.6‰

25   vs. air) occurred at the lower part of the upper oxycline (depth 65 m, O_2=32 μM) whereas within the core of the secondary nitrite maximum where the N_2O concentration fell well below saturation, N_2O was isotopically very heavy ($\delta^{15}N^{bulk}$=22.7‰ vs. air

at 400 m). In the Gulf of California, the double maximum characteristic of suboxic zones was not observed (note that a secondary nitrite maximum was also not reported at this station). Between 300 and 970 m water depths, where O_2 concentration varied from 0.6 to 3.1 μM, N_2O concentration was in the range 41.6–84.4 nM. Interestingly, isotopic

5 values varied considerably over this depth range (e.g. $\delta^{15}N^{bulk}$ was between 1.76 and 1.94‰ at 705–805 m where N_2O concentration peaked, as compared to 10.97‰ at 300 m). The conventional interpretation of these data would be that greater production of N_2O occurred through nitrification at 700 m as compared to 300 m. However, the isotopomeric measurements suggest an opposite trend according to which most of

10 the production of N_2O in the deeper waters of the Gulf of California should be through denitrification (Yamagishi et al., 2007).

Another example of N_2O behaviour in low-O_2 waters in the region comes from the work of Codispoti et al. (1992) who generated data on N_2O concentration along a section extending about 250 km offshore from Monterey Bay/Canyon, California. The

15 isotopic composition of N_2O was also determined at a station toward the shoreward end of the transect. The water was hypoxic below ~300 m, with O_2<12.5 μM between 600–800 m where N_2O concentrations exceeded 47.5 nM. The $\delta^{15}N$ and $\delta^{18}O$ values mostly hovered around those in the troposphere ($\delta^{15}N$=7.0‰ vs. air and $\delta^{18}O$=44.2‰ vs. (SMOW), but consistent maxima in both properties (e.g. up to 9‰ for $\delta^{15}N$) were

20 found within the layer of minimum O_2 and maximum N_2O. This is at variance with the above-mentioned trend observed in the Gulf of California, and shows how minor changes in O_2 concentration can result in dramatic changes in N_2O concentration and its isotopic composition (and consequently the production mechanisms).

4.4 Eastern South Pacific Ocean

25 Circulation along the western boundary of South America, described in detail by Strub et al. (1998), consists of the surface Humboldt Current carrying low-salinity and well-oxygenated Subantarctic Water (SAAW) equatorward and, the subsurface Peru-Chile

Undercurrent transporting high-nutrient, high-salinity, and low-oxygen Equatorial Subsurface Water (ESSW) poleward. The southerly and southwestly winds cause Ekman transport away from the coast, and depending on the wind intensity, bottom topography and other oceanographic conditions associated principally with remote forcing, e.g. El Nino – Southern Oscillation (ENSO), the ESSW upwells along the Peruvian-Chilean coast, bringing cold, nutrient-rich, oxygen-poor waters to the surface. The consequent high biological production sustains one of the world's most intense OMZs that extends far offshore into the open ocean from very shallow depths. The intensity and thickness of the OMZ, which is associated with the ESSW, decreases with the feature occurring progressively deeper toward the south. Thus, the most intense oxygen-deficiency occurs near Peru, where episodes of complete denitrification and associated sulphidic conditions in the water column are recorded in the literature (e.g. Dugdale et al., 1977; Codispoti et al., 1986).

4.4.1 Methane

The area off central Chile experiences upwelling and bottom-water O_2 depletion on a seasonal basis. This area has several topographic and oceanographic characteristics that set it apart from the other EBUEs. The continental shelf is quite wide here. In Austral spring and summer, intensified winds from the south and southwest make the ESSW ascend over this shelf (Sobarzo and Djurfeldt, 2004). As a result, the photic zone gets greatly enriched with nutrients, leading to high, but very variable, primary production (1–19 gC m^{-2} d^{-1}; Daneri et al., 2000) and consequently intense respiration of organic matter in bottom waters.

Methane measurements have been made since 2007 at a time-series station located over the continental shelf off Concepción, central Chile, at a water depth of ∼90 m (Fig. 7). The observed concentrations vary from 3 to 70 nM. CH$_4$ profiles usually show a significant increase from the surface (3–19 nM, 123–750% saturation) to the bottom (36–70 nM). Methane fluxes across the air-sea interface in this area are always directed from the ocean to the atmosphere and range between 0.86 and 18.7 μmol m^{-2}d^{-1}. The

emissions are maximal during upwelling periods. These values are higher than the published fluxes from the Arabian Sea (Owens et al., 1991; Bange et al., 1998; Upstill-Goddard et al., 1999; Jayakumar et al., 2001).

Temporal variability of vertical CH_4 distribution (Fig. 7) is characterized by marked seasonality, with the bottom water concentrations peaking during the upwelling-favorable periods in synchrony with a drop in O_2 levels. This is in agreement with the above-mentioned observations off Namibia, suggesting greater CH_4 diffusion from the sediment and/or smaller consumption (oxidative loss) in O_2-depleted bottom waters. However, there are times when subsurface water has lower CH_4 concentration than the surface water. These may indicate either advective input of lower methane offshore waters or a dynamic balance between production/supply and loss terms. Incubation of samples with labelled tracer yielded negative net CH_4 cycling rates, thereby providing evidence for dominance of methanotrophy (net CH_4 consumption) in the water column (Farias et al., 2009b).

4.4.2 Nitrous oxide

Off Peru and northern Chile (10° – 23° S)

The area off northern Chile and Peru experiences quasi-permanent coastal up-welling and contains one of the shallowest and most intense oceanic OMZs. A sharp oxycline, developed as the combined consequence of advection of low-O_2 ESSW and break-down of copious amounts of locally-produced organic matter, is thus located at relatively shallow depth, often within the photic zone (Paulmier et al., 2006). Below the oxycline to a depth of ~400 m, O_2 concentration is close to zero (Revsbech at al. 2009). The secondary nitrite maximum formed due to the dissimilatory reduction of NO_3^- occurs within the OMZ (Codispoti et al 1986).

As in other suboxic zones, vertical N_2O distribution in this region shows marked extrema. The concentrations are the highest (reaching up to 124 nM) within the oxycline, accounting for as much as 41–68% of the ΔN_2O pool. The minimum (10–25 nM) occurs within the secondary nitrite maximum, located between 100 and 300 m, beneath

which a secondary N_2O maximum is found as in other areas (Farías et al. 2007; also see Codispoti et al., 1992). The $\delta^{15}N$ of N_2O increases from 8.57‰ (vs. air) within the oxycline (50 m depth) to 14.87‰ (100 m depth) within the secondary nitrite maximum, the range being somewhat narrower than in the ETNP (3.6 to 22.7‰ – Yamagishi et
5   al., 2007) and the Arabian Sea (−2 to 81‰ – Naqvi et al., 2006c). Based on incubations of samples collected from the oxycline, Farias et al. (2009a) estimated N_2O production rates through denitrification (NO_2^- reduction to N_2O) ranging from 2.25 to 50.05 nmol L^{-1} d^{-1}. Nitrous oxide should also be produced by aerobic ammonium oxidation within the oxycline given that up to 42% of NH_4^+ produced in this layer is oxidized
10 by nitrifiers off northern Chile (Molina et al., 2005; Molina and Farias, 2009). However, the relative importance of these processes in N_2O production is difficult to quantify. Farias et al. (2009a) also measured N_2O consumption rates (i.e. its reduction to N_2) of between 2.73 and 70.8 nmol L^{-1} d^{-1}, with this process becoming progressively more important toward the core of the OMZ. Thus, N_2O turnover should be quite rapid.
15 Coastal waters off Peru exhibit some of the highest concentrations of N_2O observed in the ocean at or close to sea surface. Based on observations in March 1978, Elkins (1978 as cited by Codispoti et al., 1992) observed an average saturation of 632% in surface waters in the region south of about 12° S latitude. Codispoti et al. (1992) themselves found an average saturation of 450% with the maximum surface concentration
20 of 173 nM. They noted that their observations were made during a period of weak upwelling (in February–March 1985) and that higher concentrations would be expected during more vigorous upwelling. Significantly, the highest N_2O concentration in subsurface waters (175–195 nM) are from shallow, high- NO_2^- (most probably suboxic) waters (see Fig. 1b in Codispoti et al., 1992). This is very similar to observations over the
25 western Indian shelf and would support the view that such high concentrations represent transient accumulation of N_2O during denitrification at shallow depths. As in the case of the Arabian Sea, the high surface concentrations feed large efflux of N_2O to the atmosphere (12.7–30.7 μmol m^{-2} d^{-1} – Farias et al., 2009a). Codispoti et al. (1992) computed the total annual emission from their area of observations (250 000 km^2) to

Coastal hypoxia/anoxia as a source of CH_4 and N_2O

S. W. A. Naqvi et al.

Full Screen / Esc

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be 0.1 Tg N.

Off Central Chile (30°–40° S)

Regular monitoring of physical and biogeochemical conditions at the above-mentioned COPAS time series site included N_2O since its inception in 2002. The time series records show the recurrence of hypoxia/suboxia in the water column every summer (Fig. 8a). The onset of O_2 deficiency affects N-biogeochemistry both in the water column and sediments, and as in other shallow systems, a close coupling between pelagic and benthic processes is to be expected (Farías et al., 2004).

As anticipated, N_2O saturation in surface water is the highest (up to 1372%) during spring-summer upwelling period, whereas minimal values (sometimes below saturation) occur during winter. Peak accumulation of N_2O is observed mostly at mid-depth (within the oxycline) and sometimes in suboxic bottom waters, with considerable inter-annual variability. The highest concentration recorded is 245 nM. Such "hotspots" of N_2O production (Fig. 8b) occur during periods of most intense O_2 deficiency (Fig. 8a) and accumulation of NO_2^- in bottom waters (Fig. 8c) (Cornejo et al., 2007). The association of high N_2O values with varying O_2 levels point to production through nitrification as well as denitrification. Results of measurements of carbon assimilation in the dark, with and without the addition of allylthiourea, an inhibitor of monooxygenase enzymes of aerobic ammonium oxidation, and the natural isotope abundance in particulate organic carbon (δ^{13}C-POC) showed that chemolithoautotrophs and specifically aerobic ammonium oxidizers are active in the region, especially during the upwelling period, facilitating elevated production of N_2O (Farias et al., 2009b).

The onset of hypoxic/suboxic conditions affects the sediment-water exchange of dissolved nitrogen species (Farias and Cornejo, 2007). Conditions in bottom water are influenced by benthic organic remineralization, which consumes O_2 as well as other electron acceptors such as NO_3^-. Benthic fluxes of NO_3^- (2.62–5.08 mmol m^{-2} d^{-1}) and N_2O (4.46–5.53 μmol m^{-2} d^{-1}) are always directed into the sediments when hypoxic/suboxic conditions prevail in overlying waters. Nitrous oxide consumption in sediments occurs even during oxic conditions, but the rate decreases by a factor of 2.

Compared to the northern coast of Chile (off Iquique), N_2O efflux off central Chile exhibits marked seasonality (Cornejo et al., 2007). The upwelling period is characterized by emission from the ocean (1–195 μmol m^{-2} d^{-1}) with about 70% of the computed fluxes being in the vicinity of 20 μmol m^{-2} d^{-1} (averaging 24.6 μmol m^{-2} d^{-1} annually),

5 comparable to fluxes reported from other major N_2O source areas such as the Arabian Sea (3.9–15.1 μmol m^{-2} d^{-1} – Bange et al., 2001a). During the non-upwelling period (May–July), low and even negative fluxes (–9.8 to 3.7 μmol m^{-2} d^{-1}) occur, the latter indicating N_2O uptake by the ocean. The zonal distribution of N_2O flux across eastern South Pacific along latitude 32.5° S (Charpentier et al., 2009) also shows a very large

10 increase (by a factor of 30) in N_2O emissions within the coastal band off Chile.

4.5 European coastal systems

Seasonally occurring major hypoxic/anoxic events have been reported from the Adriatic Sea (see e.g. Druon et al., 2004), the coastal Baltic Sea (see e.g. Conley et al., 2007) and the northwestern shelf of the Black Sea (see e.g. Daskalov, 2003). Persistent

15 anoxia exists in the subsurface and deep waters of the Black Sea (see e.g. Konavalov et al., 2005) and the basins of the central Baltic Sea (see e.g. Conley et al., 2009; BACC Author Team, 2008). A comprehensive overview of CH_4 and N_2O measurements in European coastal waters is given in Bange (2006b). Within the context of this article we focus on the (rare) studies of CH_4 and N_2O during hypoxic/anoxic events in

20 shallow waters. Additional discussion on N_2O cycling in the Baltic Sea and Black Sea is included in Sect. 5.

4.5.1 Methane

Accumulation of CH_4 (up to 2.7 μM) in the Kiel Harbour has been observed during stagnation periods when the water column turns anoxic toward the end of the summer

25 (Schmaljohann, 1996). Since June 2006, CH_4 measurements have been performed at the Boknis Eck Time Series Station (Eckernförde Bay, Southwestern Baltic Sea) on a

monthly basis (Bergmann, 2009). Methane concentrations in the bottom layer (25 m) at Boknis Eck were up to 275 nM in June 2008; however, maximum CH_4 concentrations were not concurrent with anoxic events which usually occurred in September/October. This decoupling of anoxic events and the variability of CH_4 concentrations in the water column can be explained by CH_4-enriched groundwater seepage (Bussmann and Suess, 1998), since potential CH_4 diffusion from sedimentary sources into the water column is efficiently prevented by anaerobic CH_4 oxidation in the sediments in the Eckernförde Bay (Treude et al., 2005).

4.5.2 Nitrous oxide

At the Boknis Eck Time Series Station (Eckernförde Bay, SW Baltic Sea), N_2O has been measured on a monthly basis since July 2005 (Schweiger, 2006; Bergmann, 2009). Figure 9 shows the temporal N_2O variability during the hypoxic/anoxic event from September to October 2005. It is obvious that a pronounced N_2O accumulation occurred after the water column was ventilated in November 2005. An increase of the N_2O concentrations from 1–10 nM (in October 2005) to 16–20 nM (in November 2005) was recorded (Fig. 9). Concurrent measurements of hydroxylamine (NH_2OH), the first intermediate of NH_4^+ oxidation during nitrification, showed that maximum concentrations of NH_2OH were observable in November 2005 as well. This led to the conclusion that both N_2O and NH_2OH were formed during the re-establishment of nitrification after the re-oxygenation of the anoxic waters at Boknis Eck (Schweiger et al. 2007).

4.6 Chinese coastal waters

Because of recent economic development and population increase in Asia, coastal ecosystems in the region are subject to severe stress. Large rivers of the East and South Asian Rim are characterized by high nutrient concentrations with a skewed N/P ratio, owing most likely to extensive application of chemical fertilizers over the watersheds to support food production. As a result, depletion of dissolved O_2 commonly oc-

curs in near-bottom coastal waters of Southeast Asia including the delta of the Mekong River (63–94 μM O_2) and the Pearl River Estuary (31–63 μM O_2) (Yin et al., 2004). Similar conditions have also been reported recently from the East China Sea (ECS) off the Changjiang Estuary (e.g. Fig. 10e), with bottom-water O_2 concentrations of 63–94 μM occurring over an area of 15 000 km^2 in August 1999 (Li et al., 2002).

The Changjiang empties into the ECS with a mean water discharge of 928×10^9 m^3 yr^{-1} and total suspended matter (TSM) load of 0.35×10^9 t yr^{-1}, of which 70–80% occurs during the flood season (May–October) (Yang et al., 2002). The fresh water plume from the Changjiang disperses at the surface in the ECS (Fig. 10d) and at its peak in summer covers an area of ~85 000 km^2. In winter, the Changjiang plume is restricted to the western side of the ECS, moving southward along the Chinese coast to the South China Sea. Extensive water exchange between ECS and Kuroshio occurs across the shelf break through upwelling and frontal processes. In the broad shelf region, patchy distribution of hydrographic properties is related to distinctive source water masses (cf. Su, 1998).

4.6.1 Methane

Methane distribution in the ECS (e.g. Fig. 10a) shows a concentration gradient from the Changjiang Estuary to the Kuroshio Surface Waters with considerable seasonal and inter-annual variations (Zhang et al., 2008a). Elevated CH_4 concentrations occur in the water column of inner and mid-shelf but outside the high-turbidity plumes from the Changjiang, corresponding to the phytoplankton blooms caused by a decrease in turbidity that seems to limit photosynthesis closer to the coast (Zhang et al., 2004). Further offshore over the mid-shelf in ECS, where the water column is more stratified, CH_4 content of near-bottom samples can be 50–100% higher than at the surface. In the deeper water, data from interior of the Kuroshio show CH_4 concentrations declining with depth down to 1000 m (Zhang et al., 2004). Over the ECS shelf, the upwelled Kuroshio subsurface waters have relative low O_2 (i.e. 125–156 μM) with lower CH_4 concentrations than in near-bottom waters over the inner shelf. Thus, in the coastal

9486

waters of the ECS that are affected by eutrophication, an increase of CH_4 saturation occurs in the water column (Fig. 10a), thereby sustaining a higher sea-to-air flux of CH_4 (2.5–5.0 μmol m^{-2} d^{-1}) relative to oligotrophic waters over the open-shelf (0.5–2.0 μmol m^{-2} d^{-1}) (Zhang et al., 2004). As stated above, hypoxia develops off the Changjiang Estuary (Fig. 10e) every summer (from June to September), with the lowest O_2 levels recorded in near-bottom waters being 16–31 μM between 20–50 m isobaths in the late summer of 2003. Also, waters with O_2 concentrations ranging from 125 to 156 μM can be found at the surface over the inner-shelf of the ECS, resulting from the dispersal of plumes from the Changjiang and upwelling of offshore waters because of the combination of buoyancy and topographic effects. Concentration of CH_4 in near-bottom hypoxic waters can be as high as 30–40 nM, in comparison with the typical range of values between 10 and 20 nM in late autumn and/or early spring when the near-shore water column tends to be well mixed (Zhang et al., 2008a).

Freshwater runoff by the Changjiang appears to make a significant contribution to the CH_4 budget of the region. The concentrations in the affected area range between 15 and 130 nM with an average of 71.6 nM, and there is a positive correlation between river runoff and CH_4 concentration (Zhang et al., 2008a). This is similar to the observations off the river mouths elsewhere in the ocean, described earlier. Heterotrophic respiration in sediments overlain by hypoxic waters has been estimated to consume O_2 at a rate of 30–70 mmol m^{-2} d^{-1}, while CH_4 efflux from the sediments has been quantified as 1.7–2.2 μmol m^{-2} d^{-1}; CH_4 and O_2 appear to be negatively correlated in near-bottom waters affected by hypoxia (Zhang et al., 2008a). High surface concentrations in this region support a high sea-to-air flux, reaching up to 250 μmol m^{-2} d^{-1}, which is 20 times higher than the efflux from the shelf mixed water (10–15 μmol m^{-2} d^{-1}) and 2–3 orders of magnitude higher than the efflux from the Kuroshio Current region (<0.5 μmol m^{-2} d^{-1} – Zhang et al., 2008b).

4.6.2 Nitrous oxide

Distribution (Fig. 10b) and air – sea exchange of N_2O in the coastal region off the Changjiang Estuary and further offshore in the ECS are regulated by the prevailing hydrographic conditions (Fig. 10c–e) and nitrogen cycling. For instance, the upwelled
5 water of the Kuroshio at the shelf break is characterized by relatively low O_2 with slightly higher N_2O concentrations (20–30 nM) than surface waters of the open shelf (10–20 nM) and lower values than in the region affected by river runoff (30–40 nM) (Fig. 10b; Zhang et al., 2008b). Close to the coast, hypoxic subsurface waters having high salinity and low temperature are capped by warmer, brackish water plumes from
10 the Changjiang during the summer season (Fig. 10c, d). Concentrations of N_2O in the hypoxic layer ($O_2 < 63\ \mu M$ – Fig. 10e) can be as high as 40–60 nM as compared to 10–20 nM in the overlying surface waters and 5–10 nM at the surface further offshore over the open shelf (Zhang et al., 2008b). Where coastal hypoxia does not occur, vertical profiles of N_2O concentrations in the near-shore and open shelf regions are similar,
15 hovering around 10 nM. Off the Changjiang Estuary, ΔN_2O is positively correlated with AOU but in a non-linear mode; there also exist positive correlations between N_2O on one hand and NH_4^+ and NO_3^- on the other suggesting that N_2O is mainly produced through nitrification (Zhang et al., 2008b).

The sea-to-air flux of N_2O in the region of coastal hypoxia off the Changjiang Estuary
20 is up to 50–100 $\mu mol\,m^{-2}\,d^{-1}$, an order of magnitude higher than the values for the shelf mixed water of the ECS ($<10\ \mu mol\,m^{-2}\,d^{-1}$), Kuroshio waters ($<5\ \mu mol\,m^{-2}\,d^{-1}$) (Zhang et al., 2008b), and also the Changjiang water (20 $\mu mol\,m^{-2}\,d^{-1}$, Jing Zhang, unpublished data). Even higher fluxes to the atmosphere are expected to occur during periods when stratification is broken down by vertical mixing. Moreover, high CH_4
25 and N_2O concentrations can also be exported to the open ocean by circulation and dynamic processes across the shelf break, an important component of the "continental shelf pump" (Tsunogai et al., 1999).

4.7 Gulf of Mexico

The biogeochemistry of the northern Gulf of Mexico is greatly affected by runoff from the Mississippi River, which is the sixth largest river in the world in terms of freshwater discharge ($580 \, \text{km}^3 \, \text{y}^{-1}$ – Milliman and Meade, 1983). The enormous loading of nutrients and organic matter from land by the river in conjunction with strong near-surface stratification results in seasonal formation of a hypoxic zone that seems to be expanding with time, presently occupying an area of $22\,000 \, \text{km}^2$ at it peak during summer (Rabalais and Turner, 2006). This region is also distinguished by the occurrence of hydrocarbon seeps and gas hydrates at the seafloor, additional factors that make it important for CH_4 cycling (Brooks et al., 1981).

Supersaturation of surface waters of the Gulf of Mexico with respect to atmospheric CH_4 has long been known (Swinnerton and Lamontagne, 1974; Brooks et al., 1981). The occurrence of several subsurface maxima in the vertical profiles points to their multiple sources/formative processes such as release of CH_4 (originating from anoxic degradation of organic matter and from seeps or gas hydrates) from shelf sediments, lateral dispersal of CH_4-rich layers, and in situ production (Brooks et al., 1981). An extensive data set on CH_4 in the Gulf of Mexico hypoxic zone has been generated by Kelley (2003) on a series of cruises conducted between March 1994 and July 1998. Her results show very high CH_4 concentrations, some even matching those observed off Namibia. These high values persist during all seasons, but tend to be more elevated during summer. Also, there is no consistency in depth of occurrence of the peak value among different sites: the maximum may occur at the surface (Fig. 11a), at mid-depth (within the pycnocline, Fig. 11b) or close to the bottom (Fig. 11c). Kelley did not present O_2 data, if they were collected, but bottom-water hypoxia might have been present during the summer samplings (e.g. in case of Fig. 11b, c). The observed accumulation of CH_4 was ascribed to in situ production as a result of high concentration of particulate matter. Incubation of samples in the presence of picolinic acid (which inhibits CH_4 oxidation) provided evidence for in situ production. However, as in case of the Indian

shelf, it is quite likely that the very high values (particularly at the surface) originate from river runoff. Moreover, emission of CH_4 from the sediments coupled with low O_2 content of the bottom water may also be important contributors to the greatly elevated CH_4 levels in the water column. In addition to the role of in situ production favoured by Kelley, mid-depth maxima can also be maintained by lateral mixing/advection of high-CH_4 water and/or the loss of CH_4 from the surface layer through air-sea exchange.

There is no published information on N_2O in the Gulf of Mexico.

4.8 Tokyo Bay

A study of N_2O was carried out by Hashimoto et al. (1999) in the Tokyo Bay where hypoxia is known to develop during summer. Observations on five cruises undertaken during May–October, 1994, at a number of stations yielded high surface concentrations (averaging 11.8–90.3 nM) and saturations (166–1190%). However, these high values were apparently not related to O_2 depletion that prevailed in bottom waters during summer; instead their origin was a sewage treatment plant that generated a large amount of N_2O ($\sim$0.1 Gg N y^{-1}). In fact, the N_2O concentration decreased with depth as the bottom waters were reducing and had lost almost all NO_3^-. Anomalously high NO_2^- or N_2O values were thus not recorded, but since the gradients were sharp, it is possible that these features could have been missed due to inadequate sampling spacing in the vertical and with time [an example of extreme change in N_2O in waters approaching anoxia is provided by Rönner (1983) from the Baltic, see the following section]. The data from Tokyo Bay are similar to those from the Chesapeake Bay (also for summer) published by Elkins et al. (1978), except that the surface concentrations in the Chesapeake Bay are much lower (moderately supersaturated or undersaturated). Once oxic conditions were restored throughout the water column in October in the Tokyo Bay, both NO_3^- and N_2O increased in bottom water but still remained well below the surface values.

There is no published report on CH_4 from the Tokyo Bay.

5   Methane and nitrous oxide in anoxic zones

Land-locked or semi-enclosed basins with shallow sills connecting them with the open ocean (either directly or via another semi-enclosed sea) and having estuarine circulation (where the deep water flows into the basin over the sill and the surface water flows out) experience either permanent (Black Sea and Cariaco Basin) or intermittent (Baltic Sea and Saanich Inlet) anoxia. All four examples listed here have distinct albeit narrow (several meters thick) suboxic layers that separate deep sulphidic waters (found below the sill depth) from the oxic layers lying above it. Steep chemical gradients (chemoclines) are conspicuous features of the suboxic zone (e.g. Cohen, 1978; Walter et al., 2006; Westley et al., 2006).

5.1   Methane

One striking aspect of the biogeochemistry of these basins is the large accumulation of CH_4 in sulphidic waters (e.g. up to ~13 μM in the Black Sea (Fig. 12), 17 μM in the Cariaco Basin (Fig. 12) and 1.6 μM in the Saanich Inlet) (Kessler et al., 2005; Kessler et al., 2006a, b; Reeburgh, 2007; Ward et al., 1989). The source of CH_4 in these basins is believed to be sedimentary (Reeburgh, 2007). Kessler et al. (2005) measured ^{14}C in CH_4 in the Cariaco Basin and reported that essentially all of the CH_4 in deep waters must be from fossil sources, in spite of earlier estimates of biogenic production (Reeburgh, 1976). However, deep-water CH_4 concentrations change relatively slowly with time in the Black Sea and Cariaco Basin, while data from the Saanich Inlet show more variability related to renewal of deep water (Ward et al., 1989). Given the high deep-water CH_4 levels, surface concentrations in these basins are elevated, but not abnormally so. Cariaco Basin surface water is at or slightly above saturation with the atmosphere (Ward et al., 1987; Scranton, M. I., unpublished), while in the Black Sea, where there are some seeps, high surface CH_4 can be observed (e.g. 294% saturation observed over a 90 m deep seep in the Black Sea – Schmale et al., 2005). This indicates that most of the CH_4 emitted by the seafloor or diffusing across the

anoxic/suboxic-oxic interface is efficiently oxidized.

5.2 Nitrous oxide

Vertical distribution of N_2O in anoxic basins is significantly different from that observed in the open-ocean suboxic zones. As expected, the sulphidic layer is devoid of N_2O,
5 a feature first noticed by Cohen (1978) in the Saanich Inlet (Fig. 13), and observed subsequently in other basins as well (e.g. Hashimoto et al., 1983; Butler and Elkins, 1991; Walter et al., 2006; Westley et al., 2006). Cohen (1978) found N_2O concentration to rise up to 20.4 nM at the lower oxycline, followed by a rapid decline within the suboxic zone (<15 m thick) to reach zero/near-zero values at or just below the suboxic/anoxic
10 interface (Fig. 13). The highest concentration is much lower than observed in open-ocean O_2-deficient systems. But subsequent work has shown that this is not unusual for anoxic basins. A similar pattern of variability has been reported from the Cariaco Basin by Hashimoto et al. (1983), and from the Black Sea by Butler and Elkins (1991) and Westley et al. (2006). In fact, the peak N_2O concentrations in these basins are
15 even lower (<12 nM and <15 nM, respectively).

The spatial and temporal patterns of N_2O variability observed in the Baltic Sea are quite puzzling. The first N_2O data from this region were obtained when oxic conditions prevailed in the deep basins of the central Baltic Sea after a strong North Sea water inflow event in August/September 1977 (Rönner, 1983). In July 1979, Rönner fortu-
20 itously observed a dramatic change in N_2O concentrations at ~100 m depth at one station in the western Gotland Basin exactly when the bottom water became anoxic. This shift was associated with a decrease in N_2O concentration from 1523 nM to 0 nM within 24 h.

In a more recent study, Walter et al. (2006) investigated water-column distributions of
25 N_2O at 26 stations in the southern and central Baltic Sea in October 2003 after another major North Sea water inflow event in January 2003. By the time the observations were made, the O_2 rich North Sea water had already ventilated the formerly anoxic deep waters of the eastern Gotland Basin but had not ventilated the deep waters of

the western Gotland Basin. In the anoxic water masses of the western basins N_2O concentrations were <2 nM. The peak N_2O concentration in the overlying waters here was around 20 nM, similar to the Black Sea and Saanich Inlet. This is substantially lower than the maximum concentration of 31 nM recorded in the Bornholm Basin that had been ventilated with O_2-rich North Sea water. Walter et al. (2006) concluded that the shift from anoxic to oxic conditions after the inflow event in January 2003 had led to significant N_2O accumulation in the water column. However, the accumulated N_2O was not immediately released to the atmosphere because of the presence of a permanent halocline.

Westley et al. (2006) provided data on isotopic composition of N_2O from the Black Sea that are very intriguing in that the $\delta^{15}N$ and $\delta^{18}O$ exhibited opposite trends. Within the N_2O-maximum layer at the lower oxycline, there was a slight depletion of ^{15}N and slight enrichment of ^{18}O relative to the upper-layer mean values of 7.6‰ vs. air and 44.2‰ vs. SMOW, respectively. Much more pronounced isotopic shifts occurred within the suboxic layer where $\delta^{15}N$ fell to a minimum of -10.8‰ (the lowest ever reported from seawater) whereas $\delta^{18}O$ rose to a maximum of 67.0‰. The isotopomeric data revealed a site preference maximum that coincided with the $\delta^{18}O$ maximum. These results were interpreted to infer that both production of N_2O through oxidation of NH_4^+ diffusing upward from the anoxic layer and consumption of N_2O through denitrification were occurring within the suboxic layer, producing both depletion and enrichment of the heavier isotopes, respectively. In case of ^{15}N, depletion due to production probably overwhelmed enrichment due to consumption. However, Westley et al. did not rule out other processes such as anammox influencing N_2O cycling in the Black Sea. The above results underscore our incomplete understanding of the mechanisms of N_2O production and consumption in systems approaching and reaching complete anoxia.

6 Discussion

It is believed that most of the CH_4 accumulating in bottom waters is derived from anoxic sediments, and so the O_2 content/redox state of bottom waters is expected to affect the rate and depth of production of CH_4 in the sediment as well as its oxidative loss in the upper sedimentary column and in water itself. As described above, all O_2 deficient systems from which CH_4 data are available seem to accumulate CH_4 to varying degrees depending upon the basin morphology and the extent of O_2 deficiency in the water column. Maximal build-up (at μM levels) occurs only in truly anoxic (sulphidic) waters of the silled basins. Methane concentrations also increase in silled basins overlain by hypoxic/suboxic waters but to a much smaller extent (tens of nM). Along the open coasts, CH_4 content of bottom waters responds to changes in ambient O_2. Again the anoxic (sulphidic) bottom waters have the highest CH_4 concentrations (e.g. over the Namibian shelf), but the absolute values are influenced by water residence time, as oxidation will remove CH_4 relatively rapidly in the presence of O_2. In hypoxic or suboxic bottom waters, the pattern of CH_4 variability is not entirely consistent among various geographical areas, probably depending on local primary production and sediment composition, which are not mutually exclusive. Over the Indian shelf, the switch-over from hypoxic to suboxic conditions does not appear to have a major effect on bottom-water CH_4 content, possibly because of the deeper sulphate-CH_4 transition in the sediment, and CH_4 in bottom water increases significantly only when the sulphidic conditions develop in the water. This may be due to high reactive iron and relatively low organic carbon content of sediments. In comparison, over the Namibian shelf, bottom-water CH_4 content responds better to changes in O_2 content in the overlying water (Monteiro et al., 2006). This also seems to apply to most other systems such as the Chilean shelf, Gulf of Mexico and ECS. However, in the latter two systems, as also in case of the western Indian shelf, the situation is complicated by large allochthonous inputs of CH_4 by the rivers. Another complexity arises from in situ production of CH_4 in the water column itself, for which there is considerable circumstantial evidence (Scranton and Brewer,

1977; Scranton and Farraington, 1977; Tilbrook and Karl, 1995; Kelley, 2003; Karl et al., 2008). This is reflected by significant supersaturation in surface water in productive margins that experience upwelling but no hypoxia (e.g. Kock et al., 2008). More often than not, however, hypoxia – both natural and human induced – occurs in regions

5 of high productivity where in situ production rate in oxygenated water column is also expected to be high, and it is difficult to differentiate such production from enhanced emissions from the sediments (Scranton and Farrington, 1977).

Due to oxidative loss, accumulation of CH_4 in bottom waters does not support a large efflux to the atmosphere, except in cases of break down of stratification, episodic

10 gas eruptions, and when sedimentary inputs occur directly into the mixed layer i.e. at very shallow depths (Scranton and Farrington, 1977; Schmale et al., 2005). Therefore, an intensification or expansion of coastal hypoxic zones will probably not have a very large impact on CH_4 emissions from the ocean. More likely, an increase in productivity due to eutrophication or intensification of coastal upwelling due to global

15 warming (Bakun, 1990) may cause a greater enhancement of oceanic CH_4 emissions. At present, it is difficult to quantify or predict such changes. Nevertheless, it would be reasonable to conclude that unless CH_4 emissions are enhanced by more than an order of magnitude, the present status, where emissions from the ocean as a whole form an insignificant term in the atmospheric CH_4 budget, is unlikely to change.

20 The situation is quite different for N_2O because (1) it is mainly produced in the water column; (2) its production by all known mechanisms is enhanced at low O_2 concentrations; and (3) it has no sink in oxygenated waters. Nitrous oxide does get reduced to N_2 within cores of the suboxic zones, but the peripheries of these cores provide most suitable conditions for its production. Consequently, O_2-deficient aquatic systems are

25 invariably net producers of N_2O (e.g. Codispoti et al., 1992). However, the extent to which the loss of O_2 promotes N_2O production varies from system to system for reasons that are still not clear. The response of N_2O to deoxygenation is non-linear. The "normal" behaviour is that N_2O values peak at tens of nM level just before the environment turns reducing. Such enhancement of the N_2O yield, recorded in both (largely)

Coastal hypoxia/anoxia as a source of CH₄ and N₂O

S. W. A. Naqvi et al.

natural (e.g. off Oman) and (largely) anthropogenic (e.g. off China) hypoxic/suboxic systems, but not in anoxic basins, is mostly likely due to nitrifier denitrification (Yamagishi et al., 2007). Deviations from this behaviour, where N_2O concentrations climb up to hundreds of nM level, have been observed in three naturally-formed coastal O_2-deficient environments (off India, Peru and Chile). We predict similar abnormally high N_2O concentrations off Namibia as well. Two common features of these systems are extension of the OMZ to very shallow depths and high organic loading. The most likely way by which N_2O accumulates in very high concentrations in such settings is a more rapid reduction of NO_2^-/NO to N_2O as compared to its own reduction to N_2 by denitrifiers. This requires an inhibition of the activity of N_2O reductase. Although it has been speculated that frequent aeration due to turbulence may deactivate this enzyme from time to time in shallow, rapidly denitrifying waters (Naqvi et al., 2000), the cause of such abrupt change in N_2O cycling is not well understood and difficult to predict. Nevertheless, its significance can be gauged by the fact that the western Indian shelf, where the larger part of N_2O seems to be denitrification-derived, may alone produce up to 0.25 Tg N_2O-N annually out of the global emission of 0.86 N_2O-N yr^{-1} from the estuaries and continental shelves (Seitzinger and Kroeze, 1998). Thus, any major alterations in O_2 distribution in coastal waters are certain to have a large impact on the N_2O budget; but this effect cannot be quantified at present because of continuing uncertainties concerning the basic formative mechanisms as well as a lack of observations in key coastal regions.

Coastal hypoxia/anoxia as a source of CH$_4$ and N$_2$O

S. W. A. Naqvi et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

References

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Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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S. W. A. Naqvi et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

⏮ ⏭

◀ ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

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S. W. A. Naqvi et al.

Title Page

Abstract	Introduction
Conclusions	References
Tables	Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Coastal hypoxia/anoxia as a source of CH_4 and N_2O

S. W. A. Naqvi et al.

◄◄	►►
◄	►
Back	Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Coastal hypoxia/anoxia as a source of CH$_4$ and N$_2$O

S. W. A. Naqvi et al.

Table 1. Definitions of various stages of O$_2$ deficiency.

Stage	Criteria	Remarks
Hypoxia	$0.1 < $ O$_2$ (Winkler) ≤ 1.4 mL L^{-1} (see footnote[1]); NO$_2^-$ = 0 μM, NO$_3^-$ > 0 μM	The upper limit is based on physiological consideration. Oxygen concentrations below ~2 mg L^{-1} induce avoidance, or altered behavior, growth, reproduction or survivorship of many marine organisms (Levin et al., 2009, and references therein)
Suboxia	O$_2$ ≤ 0.1 mL L^{-1}, NO$_2^-$, NO$_3^-$ > 0 μM; H$_2$S = 0 μM	The actual O$_2$ levels are probably in the nM range (Revsbech et al., 2009). This allows reduction of elements such as N, I, Mn and Fe (but not S) with denitrification being the dominant respiratory process.
Anoxia	O$_2$ = 0 mL L^{-1}, NO$_2^-$, NO$_3^-$ = 0 μM, H$_2$S > 0 μM	The environment is completely anaerobic with sulphate reduction being the dominant respiratory process.

[1] 1 mL L^{-1} = 1.43 mg L^{-1} = 44.64 μM
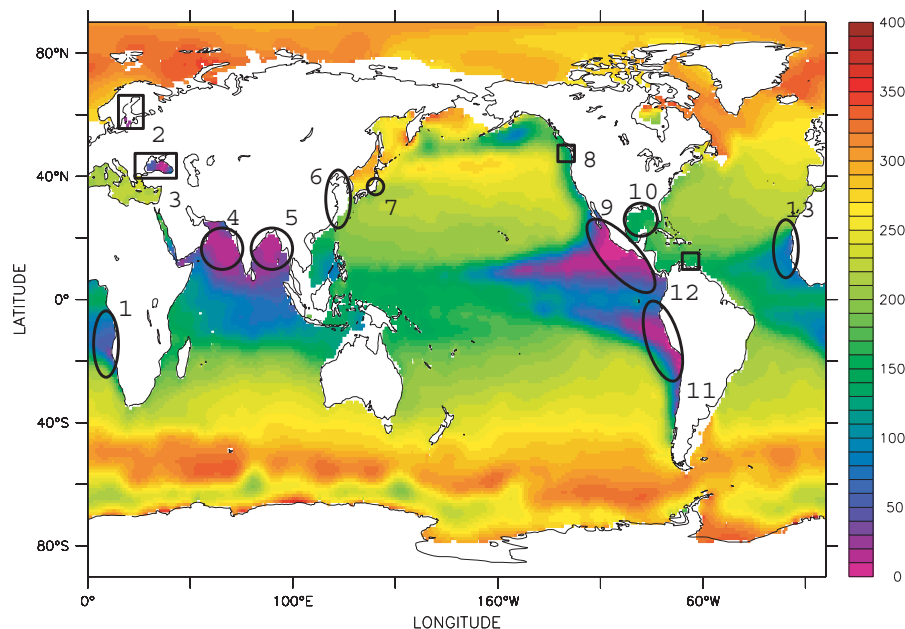
Fig. 1. Mean annual dissolved O$_2$ concentration (μmol kg^{-1}) at 150 m depth. 1°×1° gridded O$_2$ data were taken from World Ocean Atlas 2005 (Garcia et al., 2006) and converted to μmol kg^{-1}. The O$_2$-depleted zones discussed in the text are marked: 1, Off SW Africa; 2, Baltic Sea; 3, Black Sea; 4, Arabian Sea; 5, Bay of Bengal; 6, East China Sea; 7, Tokyo Bay; 8, Saanich Inlet; 9, Eastern North Pacific; 10, Gulf of Mexico; 11, Eastern South Pacific; 12, Cariaco Basin; 13, Off NW Africa. Squares depict semi-enclosed basins that experience sulphate reduction whereas circles/ovals depict other low O$_2$/hypoxic/suboxic (including seasonally anoxic) environments along open coasts.

Full Screen / Esc

Printer-friendly Version

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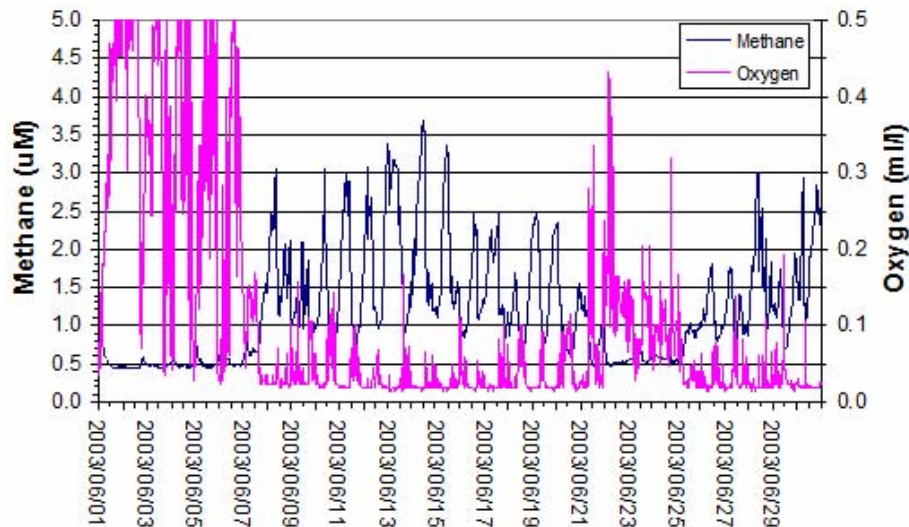
Fig. 2. Time series records of dissolved O$_2$ and methane obtained with a mooring deployed off Namibia (Lat 23° S) at 120 m water depth with sensors placed at 85 m (from Monteiro et al., 2006).
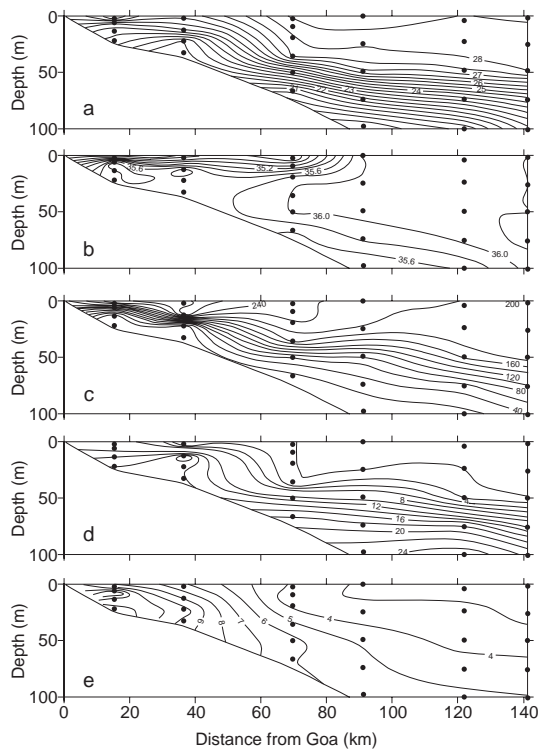
Fig. 3. Distribution of **(a)** temperature (˚C), **(b)** salinity, **(c)** O$_2$ (μM), **(d)** NO$_3^-$ (μM), and **(e)** CH$_4$ (nM) off Goa during the Southwest Monsoon (from Jayakumar et al., 2001).
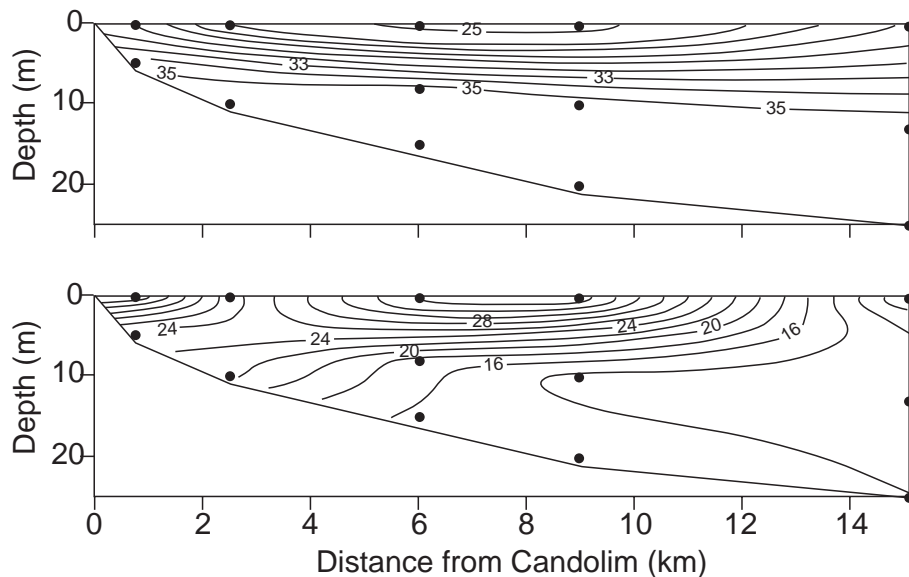
Fig. 4. Distribution of **(a)** salinity and **(b)** CH$_4$ (nM) off Goa during the Southwest Monsoon (from Jayakumar et al., 2001).
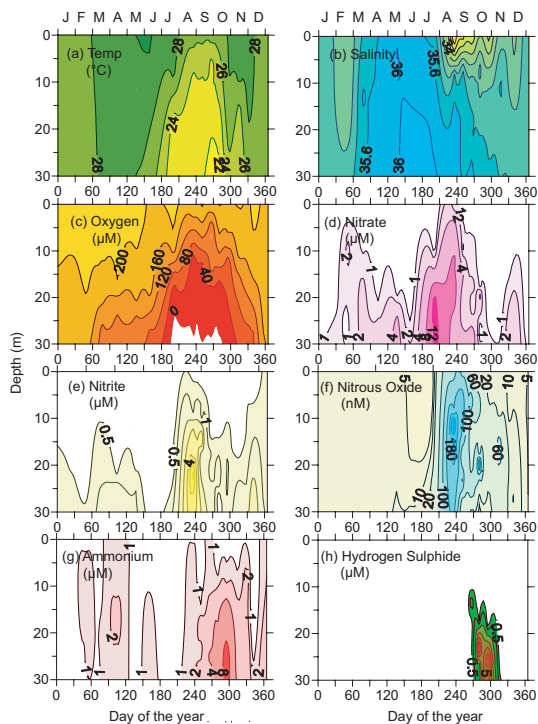
Fig. 5. Monthly-/fortnightly-averaged records showing annual cycle of **(a)** temperature, **(b)** salinity, **(c)** oxygen, **(d–g)** inorganic nitrogen species, and **(h)** hydrogen sulphide at the Candolim Time Series (CaTS) site (15°31′ N, 73°39′ E) based on observations from 1997 to 2006 (modified from Naqvi et al., 2009b).
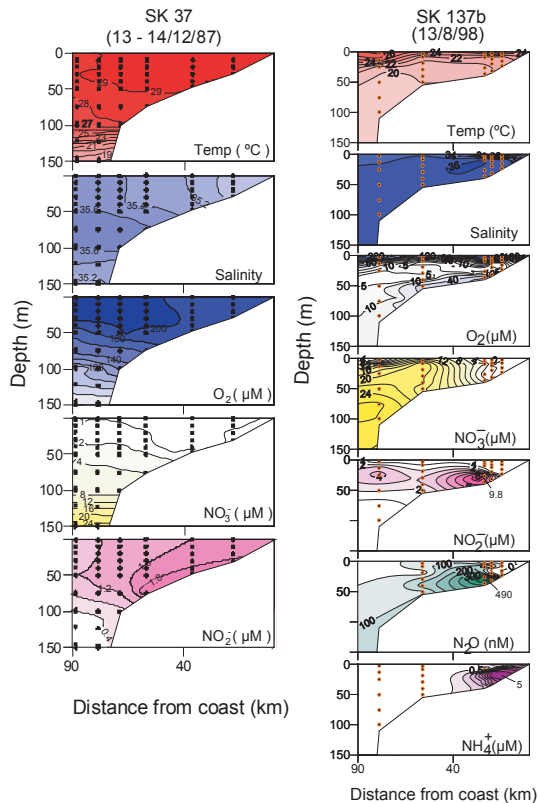
Fig. 6. Cross-shelf sections of physico-chemical properties off Mangalore during the Northeast Monsoon (left set of panels) and the Southwest Monsoon (right set of panels). Nitrous oxide was not measured on Cruise SK37, and H$_2$S was not measured on Cruise SK137, but it was present at the shoreward end of the transect (modified from Naqvi et al., 2009b).

Fig. 7. Temporal variability of CH$_4$ at the COPAS time series station located over the shelf off central Chile at a water depth of ~90 m (from Farias et al., 2009b).

Coastal hypoxia/anoxia as a source of CH$_4$ and N$_2$O

S. W. A. Naqvi et al.
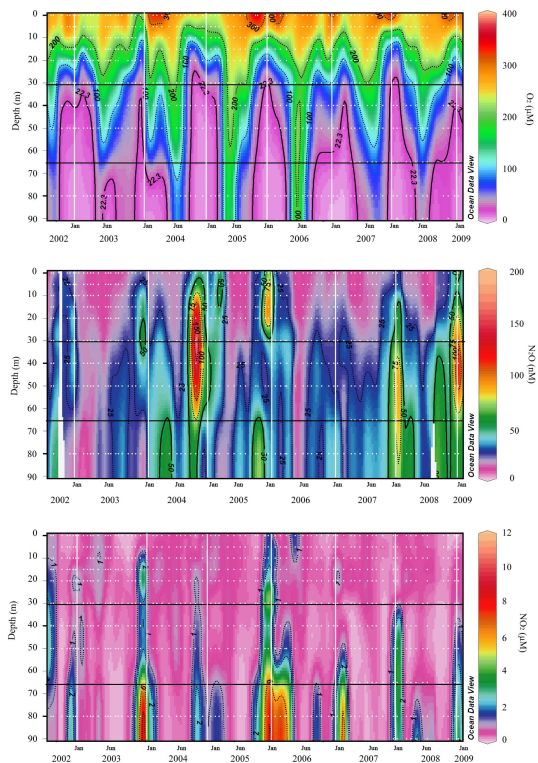
Fig. 8. Temporal variability of O$_2$ (upper panel), N$_2$O (middle panel) and NO$_2^-$ (lower panel) at the COPAS time series station (from Cornejo et al., 2007).
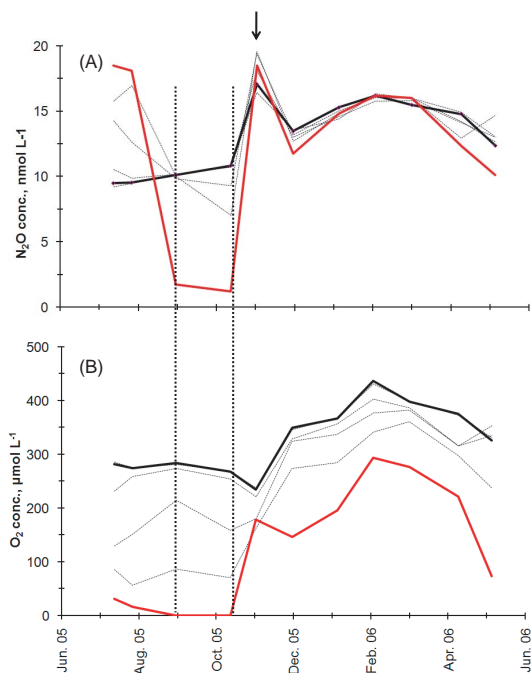
Fig. 9. Variability of N$_2$O **(A)** and O$_2$ **(B)** at Boknis Eck time series station in the western Baltic Sea from July 2005 to May 2006. The hypoxic/anoxic event is marked by vertical dashed lines. Concentrations at 1 m and 25 m are highlighted with bold black and red lines respectively. The thin dashed lines represent sampling depths of 5, 10, 15 and 20 m. The arrow marks the measurements made after the ventilation event in November 2005. Data are from Schweiger (2006).
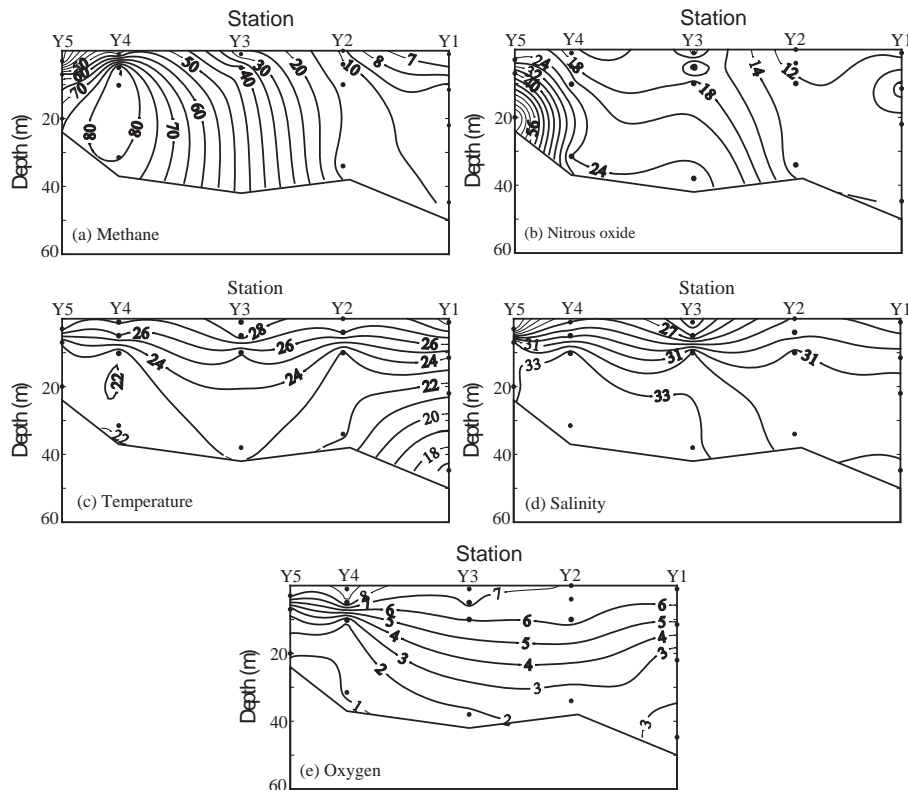
Fig. 10. Distribution of hydrographic and chemical properties in the East China Sea from a station outside Changjiang Estuary (Y5) to the Korea Strait (Y1) in September 2003: **(a)** CH$_4$ (nM), **(b)** N$_2$O (nM), **(c)** temperature (°C), **(d)** salinity, and **(e)** dissolved O$_2$ (mg/l). Data are from Zhang et al. (2008b).
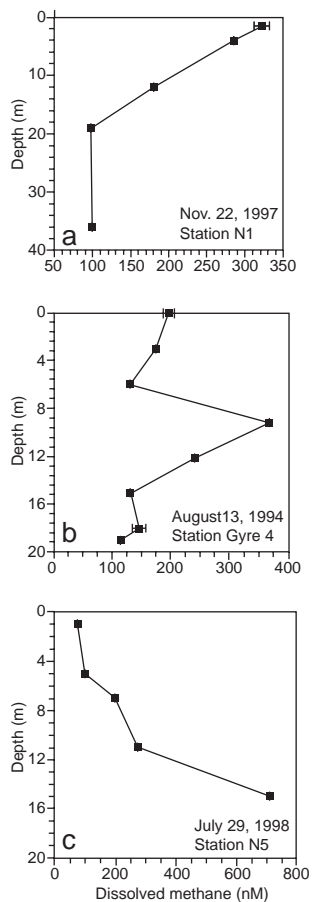
Fig. 11. Vertical profiles of CH$_4$ at three stations located over the shelf in the region affected by the Mississippi plume in the Gulf of Mexico (modified from Kelley, 2003).

Full Screen / Esc

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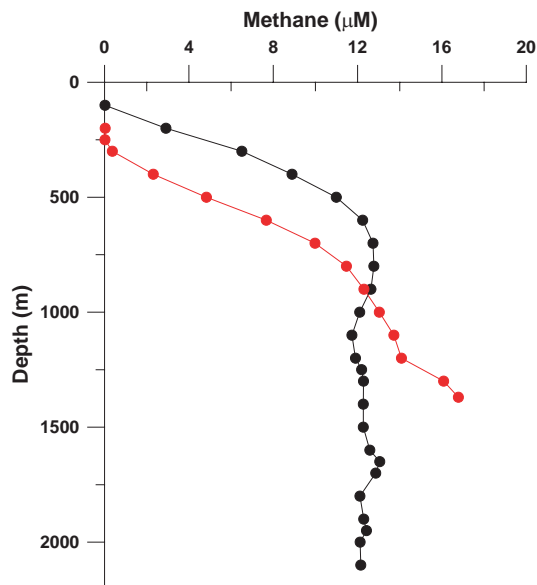
Interactive Discussion

Fig. 12. Typical vertical profiles of CH$_4$ in the Black Sea (black symbols and curve) and the Cariaco Basin (red symbols and curve). Data are from Kesseler et al. (2005, 2006a, b).

Fig. 13. Vertical profiles of **(a)** density (σ_t) and N$_2$O; **(b)** O$_2$ and H$_2$S; **(c)** NH$_4^+$ and NO$_2^-$; and **(d)** PO$_4^{3-}$ and NO$_3^-$ at two stations in the Saanich Inlet (from Cohen, 1978).

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄◄ | ►►

◄ | ►

Back | Close

Full Screen / Esc

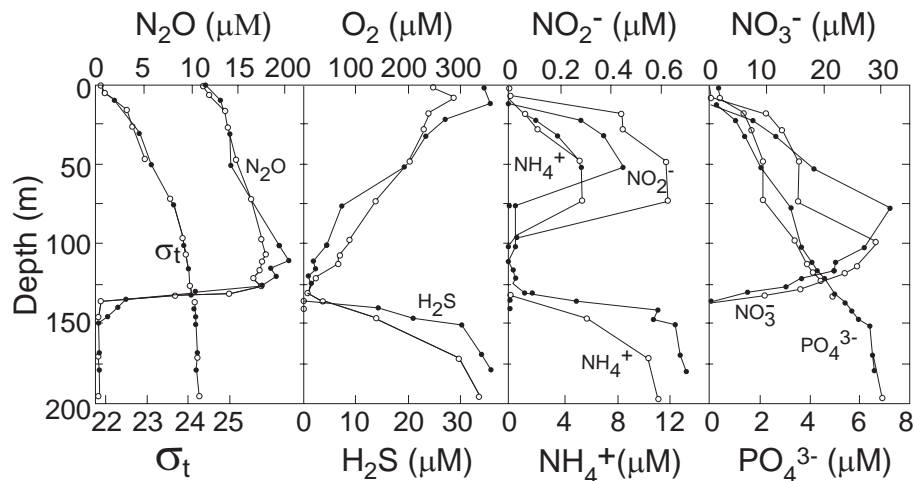Printer-friendly Version

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