

Marine hypoxia/anoxia as a source of CH₄ and N₂O

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Abstract. We review here the available information on methane (CH₄) and nitrous oxide (N₂O) from major marine, mostly coastal, oxygen (O₂)-deficient zones formed both naturally and as a result of human activities (mainly eutrophication). Concentrations of both gases in subsurface waters are affected by ambient O₂ levels to varying degrees. Organic matter supply to seafloor appears to be the primary factor controlling CH₄ production in sediments and its supply to (and concentration in) overlying waters, with bottom-water O₂-deficiency exerting only a modulating effect. High (micromolar level) CH₄ accumulation occurs in anoxic (sulphidic) waters of silled basins, such as the Black Sea and Cariaco Basin, and over the highly productive Namibian shelf. In other regions experiencing various degrees of O₂-deficiency (hypoxia to anoxia), CH₄ concentrations vary from a few to hundreds of nanomolar levels. Since coastal O₂-deficient zones are generally very productive and are sometimes located close to river mouths and submarine hydrocarbon seeps, it is difficult to differentiate any O₂-deficiency-induced enhancement from in situ production of CH₄ in the water column and its inputs through freshwater runoff or seepage from sediments. While the role of bottom-water O₂-deficiency in CH₄ formation appears to be secondary, even when CH₄ accumulates in O₂-deficient subsurface waters, methanotrophic activity severely restricts its diffusive efflux to the atmosphere. As a result, an intensification or expansion of coastal O₂-deficient zones will probably

not drastically change the present status where emission from the ocean as a whole forms an insignificant term in the atmospheric CH₄ budget. The situation is different for N₂O, the production of which is greatly enhanced in low-O₂ 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 enclosed anoxic basins. Most O₂-deficient systems serve as strong net sources of N₂O to the atmosphere. This is especially true for coastal upwelling regions with shallow O₂-deficient zones where a dramatic increase in N₂O 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 N₂O 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 N₂O as well as insufficient data from key coastal regions.

1 Introduction

Methane (CH₄) and nitrous oxide (N₂O) are two important trace constituents of the atmosphere. Both CH₄ and N₂O are potent greenhouse gases that are approximately 300 and 25 times more effective, respectively, on a per molecule basis than carbon dioxide (CO₂) in trapping heat. They also play important roles in atmospheric chemistry – CH₄ is the most abundant hydrocarbon in the atmosphere and N₂O is an important precursor for nitric oxide (NO) radicals which



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Table 1. Definitions of various stages of O₂ deficiency.

Stage	Criteria	Remarks
Hypoxia	$0.1 < \text{O}_2$ (Winkler) $\leq 1.4 \text{ ml l}^{-1}$ (see footnote ^a); $\text{NO}_2^- = 0 \mu\text{M}$, $\text{NO}_3^- > 0 \mu\text{M}$	The upper limit is based on physiological consideration. Oxygen concentrations below $\sim 2 \text{ mg l}^{-1}$ induce avoidance, or altered behavior, growth, reproduction or survivorship of many marine organisms (Levin et al., 2009, and references therein)
Suboxia	$\text{O}_2 \leq 0.1 \text{ ml l}^{-1}$, NO_2^- , $\text{NO}_3^- > 0 \mu\text{M}$; $\text{H}_2\text{S} = 0 \mu\text{M}$	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	$\text{O}_2 = 0 \text{ ml l}^{-1}$, NO_2^- , $\text{NO}_3^- = 0 \mu\text{M}$, $\text{H}_2\text{S} > 0 \mu\text{M}$	The environment is completely anaerobic with sulphate reduction being the dominant respiratory process.

^a $1 \text{ ml l}^{-1} = 1.43 \text{ mg l}^{-1} = 44.64 \mu\text{M}$

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, livestock, fossil fuel exploitation, agriculture (rice paddies) and wastewater treatment for CH₄, and agriculture (application of N-fertilizers) and fossil fuel combustion for N₂O. As a result of anthropogenic emissions, average atmospheric concentrations of CH₄ and N₂O by 2007 had risen by 156% and 19% above the pre-industrial levels to 1789 and 321 parts per billion (ppb), respectively (Anonymous, 2008).

The ocean serves as a large source of N₂O to the atmosphere, accounting for at least one third of all natural emissions (IPCC, 2007; Bange, 2006a). Although the ocean also emits CH₄ to the atmosphere, its contribution to the atmospheric CH₄ 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 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 (O₂) concentration. Containing carbon in its most reduced (−4) form, CH₄ is produced in significant quantities only in anoxic environments. In the case of N₂O (which contains nitrogen in an intermediate oxidation state of +1), both oxidative (nitrification) and reductive (denitrification) production pathways exist. Denitrification [reduction of nitrate (NO₃[−]) to elemental nitrogen (N₂) with N₂O as an intermediate] is, of course, an anaerobic process. But even in nitrification [oxidation of ammonium (NH₄⁺) to NO₃[−] where N₂O is formed as a byproduct], the yield of N₂O relative to NO₃[−] increases as the O₂ concentrations fall below about 0.5 ml l^{-1} ($\sim 22 \mu\text{M}$) (Goreau et al., 1980). Thus, changes in O₂ distribution may alter source strengths of CH₄ and N₂O. Such changes in subsurface O₂ field may be forced by altered circulation/stratification in re-

sponse 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 O₂ distribution is unclear. It has been suggested that coastal 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 O₂ deficiency) in the California Current region has been 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 decreases in the O₂ concentration in subsurface waters including an 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 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 O₂ decline in the open ocean. According to Duce et al. (2008), atmospheric deposition of anthropogenic nitrogen could have led to an increase in oceanic N₂O emission by $\sim 1.6 \text{ Tg N a}^{-1}$ ($T = 10^{12}$). While the exact mechanism of this increase is not known, some part of it might be due to enhanced production associated with O₂ 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 CH₄ and N₂O. Here we review the information available on these gases from marine systems that are affected by natural as well as human-induced O₂ deficiency. We focus on major coastal O₂-deficient zones, as well as semi-enclosed basins, while a large number of smaller water bodies (estuaries, lagoons and fjords) that also experience hypoxia on a variety of time scales (Diaz and Rosenberg, 2008; Kemp et al., 2009; Rabalais et al., 2009) are not considered.

2 Processes responsible for formation of O₂-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 the 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 O₂-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 East China Sea, Chesapeake Bay, Gulf of Mexico and Tokyo Bay is largely human-induced, whereas in the remaining regions it is primarily of natural origin.

The most important oceanic O₂-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 open ocean, severe O₂ 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 O₂ 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 boundaries of the Atlantic and Pacific oceans. They develop because of a combination of slower thermocline water renewal than in the subtropical gyres (which is why they are sometimes referred

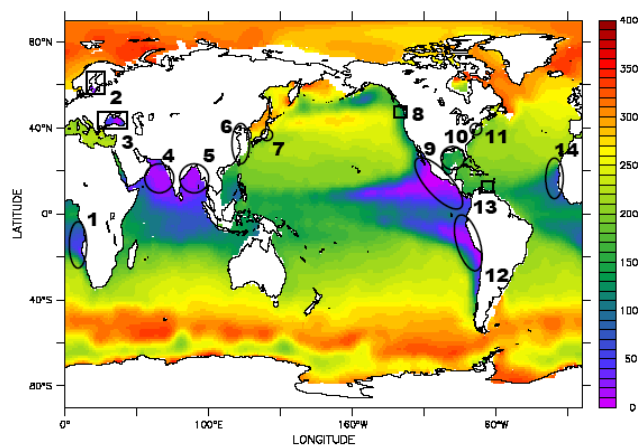


Fig. 1. Mean annual dissolved O₂ concentration ($\mu\text{mol kg}^{-1}$) at 150 m depth. $1^\circ \times 1^\circ$ gridded O₂ data were taken from World Ocean Atlas 2005 (Garcia et al., 2006) and converted to $\mu\text{mol kg}^{-1}$. The O₂-depleted zones discussed in the text are marked: 1, Off SW Africa; 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, Chesapeake Bay; 12, Eastern South Pacific; 13, Cariaco Basin; 14, Off NW Africa. Squares depict semi-enclosed basins that experience sulphate reduction whereas circles/ovals depict other low O₂/hypoxic/suboxic (including seasonally anoxic) environments along open coasts.

to as “shadow zones”) (Luyten et al., 1983) and higher O₂ 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, 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 O₂ concentrations throughout the Pacific. In all but one (off Northwest Africa) of these four eastern-boundary upwelling ecosystems (EBUEs), O₂ concentrations fall to suboxic levels. Due to its unusual geography – its 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 O₂ deficiency. Instead, the dominant variability in O₂ below the surface layer occurs in the north-south direction (Wyrski, 1971). The OMZ is particularly intense (O₂ < 0.02 ml l⁻¹, ~1 μM) and thick (between ~100/150 and 1200 m – Codispoti et al., 2001) 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 offshore OMZs to the coastal region occurs through the process of upwelling. Thus, advection of low-O₂ waters is prerequisite to (natural) development of coastal hypoxia. However, in addition to the initial O₂

content of upwelling water, intensity of O₂ deficiency over the shelf is modulated by a number of factors – local circulation/hydrography especially stratification, upwelling intensity, shelf width, and primary production – that together determine the balance between oxygen consumption 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 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 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 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 CH₄ and N₂O cycling in the ocean

3.1 Methane

The oceanic CH₄ biogeochemistry has recently been reviewed by Reeburgh (2007). Its concentrations in the open-ocean water column are generally quite low (a few nanomolar). Large CH₄ build-up does not occur even in open-ocean suboxic zones because methanogenesis, microbial production of CH₄ from CO₂ or acetate, is inhibited by the presence of other electron acceptors such as oxygen and sulphate. Conditions favouring this process usually develop in sediments where below a certain horizon (the sulphate-CH₄ transition) sulphate is almost totally depleted. Despite very high (millimolar) CH₄ concentrations below the sulphate-CH₄ interface, very low levels in the water column – the deep water is typically undersaturated with respect to atmospheric CH₄ – 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 CH₄ concentrations – close to saturation at the sea-surface 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 CH₄ paradox – has long been debated. Several explanations for the subsurface CH₄ maximum have been proposed and include both in situ production and advective transport of CH₄ produced elsewhere. For example, it has been speculated that production

within 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 CH₄ concentrations due to supply from 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 CH₄ 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). Subsequently, Damm et al. (2010) reported CH₄ production in surface waters of the central Arctic Ocean that contained sufficient phosphate but were nitrate-depleted. These authors proposed that under phosphate-replete conditions methylated compounds like dimethylsulfoniopropionate (DMSP) could be utilized by bacteria as the source of carbon. Although such a production of CH₄ as a byproduct of bacterial metabolism in aerobic waters has been shown to be thermodynamically feasible, the paradox still needs to be fully resolved.

3.2 Nitrous oxide

Bange (2008) has provided a comprehensive review of oceanic biogeochemistry of N₂O. Surface waters of the ocean are generally slightly supersaturated with respect to atmospheric N₂O (~4%; Nevison et al., 1995), but much higher supersaturation occurs in regions that experience coastal upwelling and are affected by subsurface O₂-deficiency (e.g. Bange et al., 2001a; Nevison et al., 2004). An important aspect of N₂O distribution in the ocean is the inverse relationship with O₂; this feature, recognized by early workers, prompted the suggestion that nitrification is the dominant process responsible for N₂O production (Yoshinari, 1976). Subsequently several authors reported linear relationships between $\Delta N_2O (=N_2O_{\text{observed}} - N_2O_{\text{saturation}})$ and apparent oxygen utilization ($AOU = O_2_{\text{saturation}} - O_2_{\text{observed}}$) 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 O₂ concentration does not fall below ~0.5 ml l⁻¹ after which a sharp non-linear N₂O build-up occurs as O₂ is further consumed (Codispoti and Christensen, 1985; Codispoti et al., 1992). Once the system turns suboxic, however, a depletion of N₂O 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 sensitivity of N₂O production and consumption to minor changes in O₂ in the low range has led to a

large number of studies focussing on N₂O 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; Farias and Cornejo, 2007; Cornejo et al., 2006, 2007; Farias et al., 2009a). The low N₂O concentrations within nitrite (NO₂⁻)-bearing waters are widely believed to arise from its utilization as an electron acceptor by heterotrophic bacteria (which convert it to N₂). Despite the existence of a sink for N₂O within the secondary nitrite maximum of open-ocean OMZs, these zones still serve as disproportionately large net sources of N₂O because of high N₂O 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 N₂O 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 the upper N₂O maximum in the Arabian Sea. Nicholls et al. (2006) demonstrated that this N₂O maximum is produced largely through reduction of NO₂⁻ to N₂O, but whether this reduction is carried out by denitrifiers or nitrifiers still needs to be resolved (see also Shailaja et al., 2006). Anaerobic ammonium oxidation (anammox) and dissimilatory nitrate reduction to ammonium (DNRA) are two other potential processes that can produce N₂O from NO₂⁻. However, in laboratory cultures anammox bacteria have not been found to produce significant amounts of N₂O (van der Star, 2008) and, except for one study (Lam et al., 2009), DNRA has not been considered to be a major process in the oceanic water column. In an intertidal seagrass meadow, though, DNRA by fermentative and/or sulphate-reducing bacteria was proposed to serve as a source of N₂O (Welsh et al., 2001). As we will see in the following section, the pattern of variability observed in coastal suboxic zones sometimes deviates from the trend observed in open-ocean OMZs.

4 Methane and nitrous oxide in major marine O₂-deficient zones other than enclosed anoxic basins

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 O₂ depletion does not qualify to be classified as hypoxic, because of the relatively high initial O₂ 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 wa-

ters may develop in future in this region as well (Stramma et al., 2008).

Kock et al. (2008) carried out extensive measurements of CH₄ 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 upwelled water. The annual CH₄ emission from the region was quantified as 1.6–2.9 Gg CH₄, which is not very significant in comparison to global supply to the atmosphere.

There are at present no published data on N₂O from this area. However, in October–November 2002, Walter et al. (2004) measured N₂O in surface waters along a transect at 10° N. At the eastern end of the transect, over the African shelf to the south of the Mauritanian upwelling zone, N₂O saturation reached a maximum of 113%, which was ascribed to N₂O supply by river or ground waters.

4.1.2 Off Southwest Africa

Upwelling off Southwest Africa (Namibia) supports the highest primary production rates of all the four major EBUEs (Carr, 2002), and degradation of copious organic matter in the water column and shelf sediments culminates in the occurrence of sulphidic conditions in bottom waters extending offshore to the shelf edge off the Walvis Bay (Chapman and Shannon, 1985; Brüchert et al., 2006, 2009; van der Plas et al., 2007; Lavik et al., 2009). In addition to respiration of locally-produced organic matter, the intensity of O₂ deficiency is also modulated by the initial O₂ 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 O₂ 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 O₂ 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 N₂O in the water column in this area. On the other hand, CH₄ biogeochemistry in the region has attracted considerable attention largely due to “gas eruptions” (presumably a mixture of CH₄ and hydrogen sulphide (H₂S)) 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

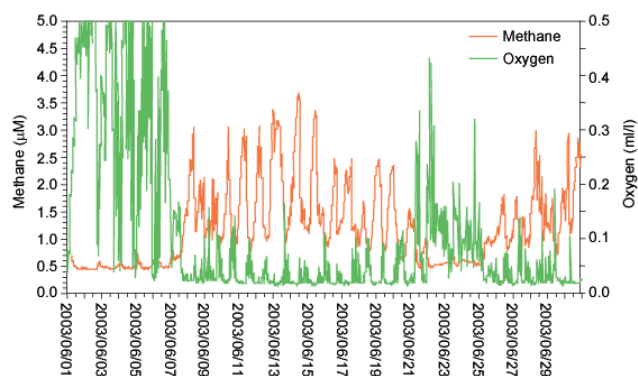


Fig. 2. Time series records of dissolved O₂ (green) and methane (orange) obtained with a mooring deployed off Namibia (Lat 23° S) at 120 m water depth with sensors placed at 85 m. Data are from Monteiro et al. (2006).

sedimentary profiles of CH₄ have been published from the region (water depths 27–109 m – 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 relatively shallow depths (tens of centimeters to a few meters). Accordingly, H₂S and CH₄ accumulate in porewaters in high concentrations (to ~22 and 8 mM, respectively – 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/ebullition and diffusion in supplying these gases to the overlying water column is not quite clear. Emeis et al. (2003) 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 H₂S can be explained by diffusive fluxes alone (Brüchert et al., 2006, Lavik et al., 2009). This probably applies to CH₄ as well.

Scranton and Farrington (1977) investigated distribution of CH₄ in the water column off Walvis Bay and recorded high values (reaching up to 879 nM) both close to the surface and in near-bottom 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 CH₄ concentrations (forming a minimum) probably resulted from the advection of off-shore water. The high concentrations in near-surface waters could arise from inputs from sediments at very shallow depths followed by lateral mixing/offshore advection of

CH₄-rich waters. However, Scranton and Farrington (1977) opined that some in situ production of CH₄ was probably also occurring in the upper water column. Very recently Brüchert et al. (2009) have provided additional chemically-measured CH₄ data from four stations over the shelf (water depths 27–67 m) that were occupied repeatedly from May 2001 to May 2004. Methane concentrations observed by these authors were even higher – up to 2.9 µM at the surface and 5.2 µM at depth at the shallowest station. To our knowledge, these concentrations are by far the highest reported from any open coastal region.

Results of a high-resolution (hourly) time series, obtained with a mooring having O₂ and CH₄ 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 detected until the O₂ content had declined to 0.2 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 O₂ concentration. The seasonal-scale CH₄ enrichment in bottom waters is modulated by event-scale advection of water as well as by daily-time-scale fluxes of O₂. 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 matter.

4.2 Northern Indian Ocean

The northern Indian Ocean comprises two major basins, the Arabian Sea in the northwest 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 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, Yemen and Oman) and eastern (off India) boundaries (Naqvi et al., 2006a). Both the Arabian Sea and the Bay of Bengal experience severe oxygen depletion at mid-depths. While the minimum O₂ concentrations determined by the Winkler method do not differ by more than 0.05 ml l⁻¹ (~2 µM), this subtle difference is responsible for the prevalence of contrasting redox conditions in the two basins: Unlike the Arabian Sea, a secondary nitrite maximum associated with denitrification is not observed in the Bay of Bengal. Consequently, NO₃⁻ concentrations within the core of the OMZ are 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 also smaller in the Bay of Bengal than in the Arabian Sea. Since the northern Indian Ocean is surrounded by land masses on three sides and the O₂ deficiency extends over a wide depth range, the OMZs impinge upon a very large area of the continental margin in this region: as much as two-thirds of the global

continental margin area in contact with bottom waters having O₂ < 0.2 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 Tg N a⁻¹ – Naqvi et al., 2010a). 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 upwelled water does not reach sufficiently close to the surface. By contrast, O₂-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) Water upwelling in the western Arabian Sea is derived from the south and has relatively high initial O₂ 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 O₂ 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 the 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). However, 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 O₂ content marginally above suboxia. Thus, the combination of sluggish upwelling, low initial O₂ content of the upwelled water, wide shelf, and very strong thermohaline stratification at very shallow depths leads to the formation of the largest natural coastal hypoxic zone (area ~200 000 km²) anywhere in the world (Naqvi et al., 2000). It is thus best suited to investigate the effect of coastal hypoxia on the cycling of CH₄ and N₂O.

4.2.1 Methane

High saturations of CH₄ (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 CH₄ distribution at the sea surface. Therefore, even though the bottom waters over the Omani shelf may sometimes become hypoxic during the late Southwest Monsoon (Naqvi et al., 2010b), the contribution of hypoxia in maintaining observed high surface CH₄ concentrations cannot be evaluated. However, as elevated CH₄ concentrations also occur in upwelled waters outside hypoxic zones (e.g. off Mauritania – Kock et al., 2008), at least a part of CH₄ 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; Codispoti et al., 2001). Yet, the upper layer CH₄ 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 CH₄ 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 CH₄ section along with corresponding sections of temperature, salinity, oxygen and nutrients off 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 O₂ deficiency within a few meters of the sea-surface (Fig. 3c).

The most striking feature of CH₄ distribution (Fig. 3e) is the sharp onshore-offshore gradient with 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 close to the coast as evident from the association of peak CH₄ values (reaching up to 48 nM, corresponding to over 2500% saturation) with the low-salinity cap observed along a closely-sampled shallow transect off Goa (Jayakumar et al., 2001). Even higher CH₄ levels (up to 248 nM, ~13 000% saturation at ~15 salinity) were recorded by these authors within the Mandovi Estuary. Thus, over the inner shelf (water depths generally <20 m), CH₄ maximum is located at/near the surface, although concentrations remain elevated even below the pycnocline, which in part may be due to some vertical mixing. At greater water depths, the highest values are found close to the bottom, indicating CH₄ emission from shelf sediments

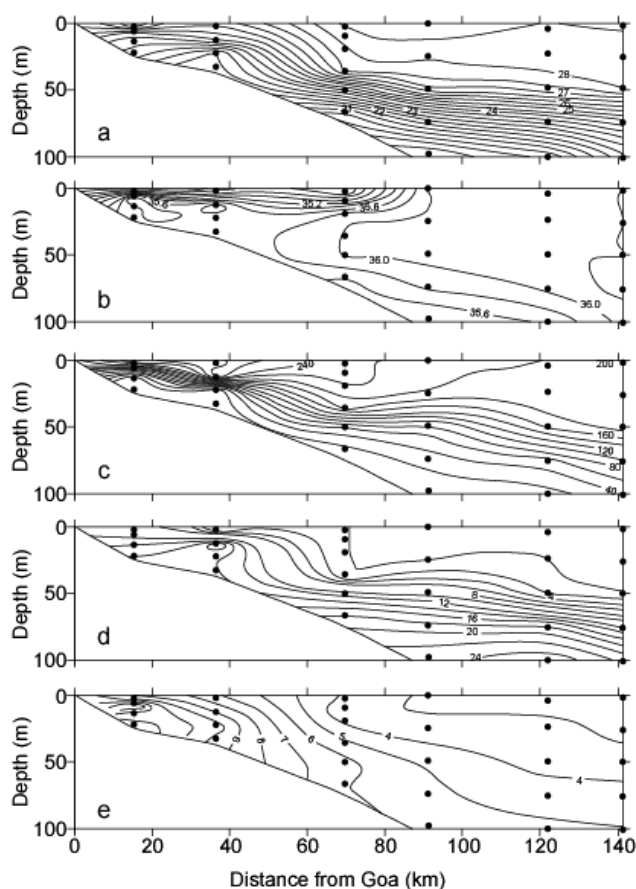


Fig. 3. Distribution of (a) temperature (°C), (b) salinity, (c) O₂ (µM), (d) NO₃⁻ (µM), and (e) CH₄ (nM) off Goa (~15.5° N, 73.75° E) during the Southwest Monsoon. Reproduced with permission from Jayakumar et al. (2001).

to the overlying water column. Nevertheless, the observed concentrations are not anomalously high (generally <10 nM) and are comparable to maximal CH₄ concentrations in the upper water column of the open Arabian Sea (Owens et al., 1991; Jayakumar et al., 2001). However, a significant shift in CH₄ distribution is observed with the appearance of H₂S in bottom waters. This usually happens by late August/early September when nitrate gets fully consumed through denitrification/anammox over the inner- and mid-shelf regions (at water depths of approximately 20–50 m) (Naqvi et al., 2006b, c). The sulphidic bottom waters have been found to contain over 40 nM CH₄ (Gayatree Narvenkar, unpublished data).

The source of CH₄ 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 CH₄ trapped in such sediments over the inner continental shelf has been estimated as 2.6 Tg

(Karisiddaiah and Veerayya, 1994). However, there has not been any observation of significant CH₄ emission from sediments through bubble ebullition in the region. In any case, the above-mentioned CH₄ inventory does not appear to be sufficient to sustain the observed CH₄ supersaturation in the overlying waters (Jayakumar et al., 2001).

There are few data on CH₄ distribution in sedimentary porewaters off the Indian coast, but the sulphate-CH₄ 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 micromolar) 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 methanogenesis do not seem to occur in the upper few tens of centimeters in sediments. However increased hypoxia in this area, with accompanying increases in carbon flux and lower O₂, would likely increase the importance of sulphate reduction and CH₄ production within the sediments.

Given the large geographical changes in surface saturation and wind speed, the computed fluxes of CH₄ from the Arabian Sea vary greatly (from ~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, 1999). Despite these high fluxes, the highest estimate of CH₄ emission from the Arabian Sea as a whole is only 0.1–0.2 Tg a⁻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, reflecting inputs by river water. This is consistent with high CH₄ 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 (<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 CH₄ from the sediment underlying hypoxic waters could be occurring over this segment of the shelf. The observed CH₄ 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 vegetation in the world (the Sundarbans), but then the observations were not made during periods of highest river runoff.

4.2.2 Nitrous oxide

High N₂O 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 N₂O 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 high concentration of N₂O in the upwelling water, which is not suboxic (Naqvi, 1991, 1994) and contains high dissolved N₂O (Bange et al., 2001b). Observations at 12 stations located over the Omani shelf during September 2004 (S. W. A. Naqvi, unpublished data) yielded surface N₂O concentrations ranging from 9.7 to 24.7 nM (156–358% saturation), consistent with previous results. However, depth profiles of N₂O 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 N₂O.

The western continental shelf of India is one of the most interesting and important oceanic sites for N₂O cycling; arguably it is also the best studied. Distribution of N₂O over various segments of the coast using data collected on a number of cruises has been investigated (Naqvi et al., 1998, 2000, 2006a, b, c, 2009). In addition, measurements of N₂O 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. 4.

During the Northeast Monsoon and Spring Intermonsoon periods, when the water column over the Indian shelf is well oxygenated (Fig. 4c), N₂O concentrations do not exceed 10 nM (Fig. 4f). Nitrous oxide begins to accumulate as O₂ is consumed in the subsurface layer after the onset of Southwest Monsoon upwelling (usually in June). The concentrations continue to rise even after the system becomes suboxic. In fact, the greatest build-up of N₂O coincides with the rapid decline in NO₃⁻ (Fig. 4d) and accumulation of NO₂⁻ (Fig. 4e), pointing to N₂O 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 N₂O. However, the concentrations decrease rapidly once the environment becomes sulphate reducing (Fig. 4h), which indicates that the observed high concentrations cannot be due

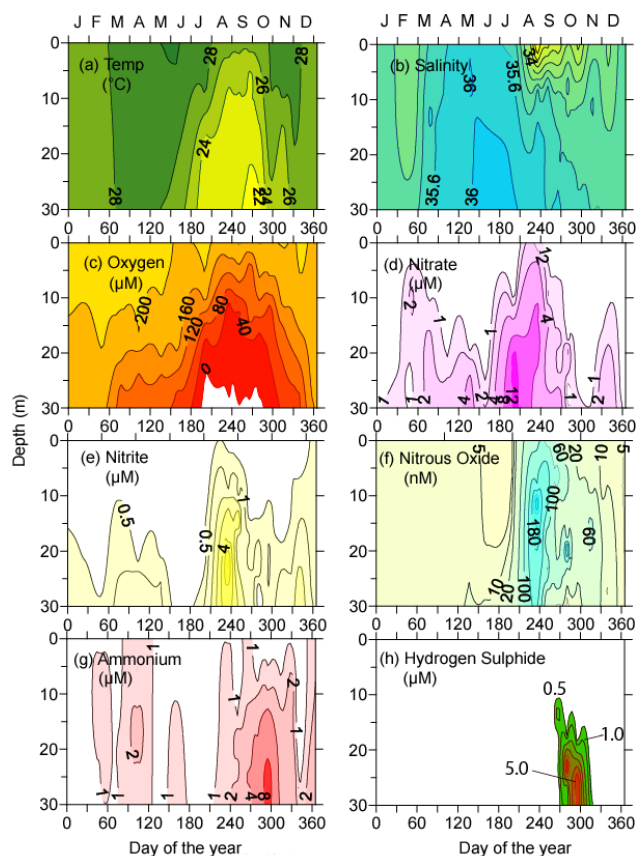


Fig. 4. Monthly-/fortnightly-averaged records showing annual cycle of (a) temperature, (b) salinity, (c) oxygen, (d–g) inorganic nitrogen species, and (h) hydrogen sulphide at the Candolim Time Series (CaTS) site (15.52° N, 73.65° E) based on observations from 1997 to 2006. Modified from Naqvi et al. (2009).

to inhibition of N₂O reductase activity by H₂S (Senga et al., 2006).

Observations along cross-shelf transects also show a similar pattern of N₂O variability (Naqvi et al., 2000, 2006b, c, 2009). During the Northeast Monsoon N₂O concentrations are low and less variable (<25 nM to a depth of 100 m). But the onset and intensification of O₂ deficiency through the summer (Southwest Monsoon) brings about dramatic changes in the N₂O field. By late summer/early autumn one can identify three zones with different redox conditions prevailing in bottom waters north of about 12° N latitude: hypoxia over the outer shelf (offshore of 50/60-m water depth), suboxia over the mid shelf (between 50/60-m and 20/30-m water depths), and anoxia over the inner shelf (between 20/30-m and 10-m water depths). Both the highest and the lowest N₂O concentrations are associated with reducing environments. The highest recorded value (765 nM off Goa – Naqvi et al., 2006c), for example, came from a sample that had lost most of its NO₃⁻ through denitrification. In addition to the association of high N₂O and NO₂⁻ (up to 16 μM)

values, accumulation of N₂O during denitrification has also been demonstrated by Naqvi et al. (2000) through incubation in air-tight bags of water samples that were initially close to but not quite suboxic (O₂ ~ 15 μM). It was suggested by these authors that frequent aeration of the water through turbulence could suppress the activity of N₂O reductase allowing transient production of N₂O. In regions where, and during periods when, subsurface O₂-deficiency is not severe enough to allow the onset of suboxic conditions, as happens off the southwest coast of India (generally south of ~12° N latitude), abnormally high (>100 nM) N₂O concentrations 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 N₂O from the Indian shelf is thus computed to be 0.05–0.38 Tg N₂O for the upwelling season. For comparison, the total annual efflux of N₂O 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-O₂ 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, 2009). Because N₂O data from this region go back only to 1997, it is not clear to what extent has this intensification affected N₂O cycling. However, given the observation that the highest N₂O concentration is observed when O₂ deficiency is the most intense, we speculate that an increase in production is likely to have occurred relative to earlier 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 N₂O show a single broad maximum within the OMZ (Naqvi et al., 1994). Surface saturations (89–214%) and atmospheric fluxes (–0.10 to 10.67 μmol m⁻² d⁻¹) 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. As a result the upwelled water does not reach very shallow depths (Naqvi et al., 2006a), and maximal N₂O concentrations over the shelf are a few tens of nanomolar (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 the northwesterly winds drive intense upwelling along the west coast of the United States and the northwest coast of Mexico. An extensive OMZ with O₂ < 0.2 ml l⁻¹ (9 μM) 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-O₂ concentrations also extend at mid-depths quite far north off the west coast of United States (especially in the silled basins of California Borderland), although the water column does not seem to be reducing (e.g. Sigman et al., 2003). As already mentioned, large decreases in subsurface O₂ concentrations in the California Current System have been recorded recently. These are believed to result from advection of O₂ depleted water over the shelf (Grantham et al., 2004; Bograd et al., 2008; Chan et al., 2008; Connolly et al., 2010).

4.3.1 Methane

The open-ocean suboxic zone of the eastern tropical North Pacific (ETNP) contains the largest pool of CH₄ in the open ocean, although the computed sea-to-air flux from this region (0.77–3.0 μmol m⁻² d⁻¹) is quite modest (Sansone et al., 2001). Vertical CH₄ 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) CH₄ maximum outside the 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 CH₄ through microbial activity associated with suspended particles recycled by zooplankton grazing. It may be noted that a secondary particle (turbidity) maximum was also found within suboxic waters. A subsequent study by Sansone et al. (2001) in the ETNP along a transect extending offshore from the Mexican coast also found relatively higher CH₄ concentrations in the suboxic layer (Fig. 5c). 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 CH₄ and concluded that while CH₄ 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 recent study, Sansone et al. (2004) focused on CH₄ cycling along the western Mexican continental margin in and around the Gulf of California (Fig. 6c, d). Their sampling stations were positioned both in the coastal basins and over the open margins. Those stations where water depth exceeded the

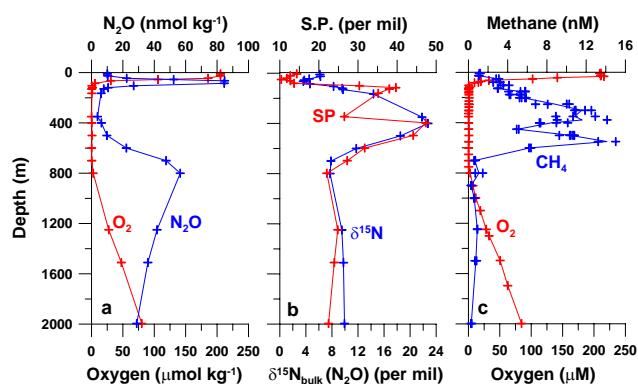


Fig. 5. Vertical profiles of dissolved O₂, N₂O and CH₄ concentrations, δ¹⁵N of N₂O and Site Preference (SP) of ¹⁵N in N₂O at a station located within the open-ocean suboxic zone of the eastern tropical North Pacific (16° N, 107° W). Data are from Sansone et al. (2001) for CH₄ and from Yamagishi et al. (2007) for N₂O.

lower boundary of the OMZ had lower CH₄ concentrations than the station where the OMZ impinged upon the seafloor, consistent with higher CH₄ supply to and/or lower oxidative loss within the OMZ. The highest build-up of CH₄ (up to 78 nM) was found to occur in bottom waters of silled basins (Fig. 6d), presumably through diffusion from the seafloor. Apparently this did not affect CH₄ distribution outside the basins, perhaps because of water column CH₄ oxidation. Diffusive fluxes from the sediment (0.24–5.5 μmol m⁻² d⁻¹) computed from porewater CH₄ gradients were 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 CH₄ in the water column is also required to sustain the sea-to-air flux.

Several studies have been conducted on CH₄ cycling in coastal waters further north in the California Current System (e.g. Ward, 1992; Cynar and Yayanos, 1992, 1993; Tilbrook and Karl, 1995; Kessler et al., 2008). The usual trend of CH₄ 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 CH₄ maxima, particularly because there is significant 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 CH₄ emission from hydrocarbon seeps. Radiocarbon measurements confirmed the importance of seep-derived CH₄ in the Santa Barbara Basin (Kessler et al., 2008). Due to high CH₄ concentration in subsurface waters, upwelling enhances supersaturation in surface waters (Rehder et al., 2002).

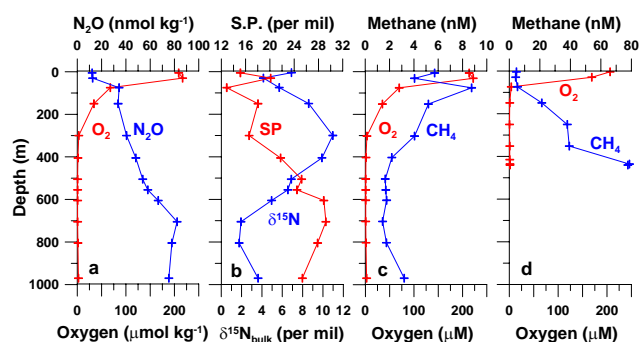


Fig. 6. (a–c) Vertical profiles of dissolved O₂, N₂O and CH₄ concentrations, δ¹⁵N of N₂O and SP of ¹⁵N in N₂O at an open margin station in the Gulf of California (26.3° N, 110.13° W); (d) Vertical profiles of dissolved O₂ and CH₄ at a silled-basin station (sill depth 50 m) in the same region (21.3° N, 105.9° W). Data are from Sansone et al. (2001, 2004) for CH₄ and from Yamagishi et al. (2007) for N₂O.

4.3.2 Nitrous oxide

Early studies of N₂O in the ETNP were undertaken by Cohen and Gordon (1978) and by Pierotti and Rasmussen (1980). Surface waters were found to be generally supersaturated with respect to atmospheric N₂O (on an average by 111% and 123% in the two studies), driving a flux of N₂O from the ocean to the atmosphere. Vertical N₂O profiles, more comprehensively examined by Cohen and Gordon (1978), revealed the existence of double maxima in the region affected by denitrification. This was attributed to consumption of N₂O 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 N₂O (Yoshinari et al., 1997; Yamagishi et al., 2007). Yamagishi et al. (2007) presented data from two stations – one each located within the heart of the suboxic zone of the ETNP (Fig. 5a, b) and the central Gulf of California (Fig. 6a, b) – on N₂O concentration and its isotopic composition. The latter also included isotopomeric analysis (i.e. the location of ¹⁵N in linear N₂O molecule) which provides information on the mechanisms of N₂O production. In the ETNP, the highest N₂O concentration (~87 nM, Fig. 5a) and the lowest isotopic values (e.g. δ¹⁵N_{bulk}=3.6‰ vs. air, Fig. 5b) occurred at the lower oxycline (depth 65 m, O₂=32 μM) whereas within the core of the secondary nitrite maximum where the N₂O concentration fell well below saturation, N₂O was isotopically very heavy (δ¹⁵N_{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 O₂ concentration varied from 0.6 to 3.1 μM, N₂O concentration was in the range 41.6–84.4 nM (Fig. 6a). Interestingly, isotopic values (Fig. 6b) varied considerably

over this depth range (e.g. $\delta^{15}\text{N}^{\text{bulk}}$ was between 1.76 and 1.94‰ at 705–805 m where N₂O reached peak values, as compared to 10.97‰ at 300 m). The conventional interpretation of these data would be that greater production of N₂O occurred through nitrification at 700 m as compared to 300 m. However, isotopomeric measurements suggest an opposite trend according to which most of the production of N₂O in deeper waters of the Gulf of California should be through denitrification (Yamagishi et al., 2007).

Another example of N₂O behaviour in low-O₂ waters in the eastern North Pacific comes from the work of Codispoti et al. (1992) who generated data on N₂O concentration along a section extending about 250 km offshore from Monterey Bay/Canyon, California. The isotopic composition of N₂O was also determined at a station toward the shoreward end of the transect. The water was hypoxic below ~300 m, with O₂ < 12.5 μM between 600–800 m where N₂O concentrations exceeded 47.5 nM. The $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values mostly hovered around those in the troposphere ($\delta^{15}\text{N}=7.0\text{‰}$ vs. air and $\delta^{18}\text{O}=44.2\text{‰}$ vs. SMOW), but consistent maxima in both properties (e.g. up to 9‰ for $\delta^{15}\text{N}$) were found within the layer of minimum O₂ and maximum N₂O. This is at variance with the above-mentioned trend observed in the Gulf of California, and shows how minor changes in O₂ concentration can result in dramatic changes in N₂O concentration and its isotopic composition (and consequently the production mechanisms).

Estimates of sea-to-air fluxes from the ETNP vary over a wide range. Cohen and Gordon (1978) reported an average efflux of 2.75 μmol m⁻² d⁻¹ (range -0.79–5.5 μmol m⁻² d⁻¹), which is substantially lower than the corresponding estimate (10.6 μmol m⁻² d⁻¹) of Pierotti and Rasmussen (1980). Using the same data set (of Pierotti and Rasmussen), however, Cohen and Gordon (1978) computed an average efflux of 6.68 μmol m⁻² d⁻¹ between 4 and 22° N latitudes. Accordingly, the estimate for total N₂O emission from the ETNP by these authors should also be scaled down to 0.75 Tg N₂O a⁻¹. For comparison, the average value of Cohen and Gordon (1978) when applied to the same area yields an emission estimate of ~0.3 Tg N₂O a⁻¹.

4.4 Eastern South Pacific Ocean

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 south-westerly 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 Niño – Southern Oscillation (ENSO) (Shaffer et al., 1999), 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 O₂-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 O₂ 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 the 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 g C 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. 7a). The observed concentrations vary from 3 to 70 nM. Methane 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, ranging between 0.05 and 59.5 μmol m⁻² d⁻¹ (mean 25.6 μmol m⁻² d⁻¹ – L. Farias, unpublished data) 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 CH₄ distribution (Fig. 7a) is characterized by marked seasonality, with the bottom water concentrations peaking during the upwelling-favorable periods in synchrony with a drop in O₂ levels. This is in agreement with the above-mentioned observations off Namibia, suggesting greater CH₄ diffusion from the sediment and/or smaller consumption (oxidative loss) in O₂-depleted bottom waters. However, there are times when subsurface water has lower CH₄ concentration than surface water. These may indicate either advective input of lower CH₄ offshore waters or a dynamic balance between production/supply and loss terms. Incubation of samples with labelled tracer yielded negative net CH₄ cycling rates, thereby providing evidence for dominance of methanotrophy (net CH₄ consumption) in the water column (Farias et al., 2009b).

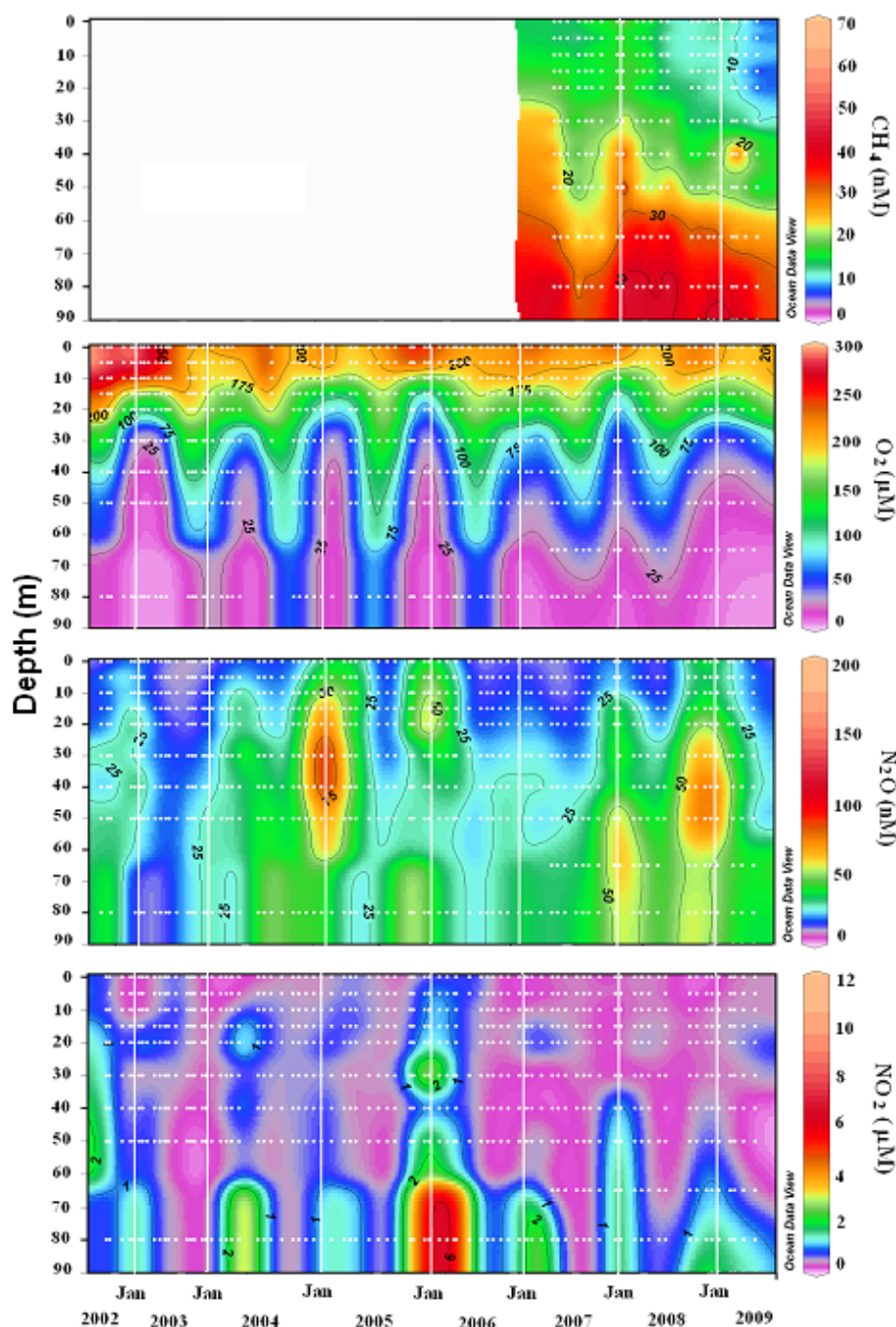


Fig. 7. Temporal variability of (a) CH₄, (b) O₂, (c) N₂O; and (d) NO₂⁻ at the COPAS time series station located over the shelf off central Chile at a water depth of ~90 m. Data are from Farias et al. (2009b) for CH₄ and from Cornejo et al. (2007) for other parameters.

4.4.2 Nitrous oxide

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

The area off northern Chile and Peru experiences quasi-permanent coastal upwelling and contains one of the shallowest and most intense oceanic OMZs. A sharp oxycline, developed as the combined consequence of advection of low-

O₂ ESSW and break-down of copious amounts of locally-produced organic matter, is thus located at relatively shallow depths, often within the photic zone (Paulmier et al., 2006). Below the oxycline to a depth of ~400 m, the O₂ concentration is close to zero (Revsbech et al., 2009). The secondary nitrite maximum formed due to dissimilatory reduction of NO₃⁻ occurs within the OMZ (Codispoti et al., 1986).

As in other suboxic zones, vertical N₂O distribution in this region shows marked extrema. The concentrations are the highest (reaching up to 86 nM) within the oxycline, accounting for as much as 41–68% of the ΔN₂O pool. The minimum (10–25 nM) occurs within the secondary nitrite maximum, located between 100 and 300 m, beneath which a secondary N₂O maximum is found as in other areas (Fariás et al., 2007; also see Codispoti et al., 1992). The δ¹⁵N-N₂O 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 al., 2007) and the Arabian Sea (–2 to 81‰ – Naqvi et al., 2006c). Based on incubations of samples collected from the oxycline, Fariás et al. (2009a) estimated N₂O production rates through denitrification (NO₂[–] reduction to N₂O) 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 NH₄⁺ produced in this layer is oxidized by nitrifiers off northern Chile (Molina et al., 2005; Molina and Fariás, 2009). However, the relative importance of these processes in N₂O production is difficult to quantify. Fariás et al. (2009a) also measured N₂O consumption rates (i.e. its reduction to N₂) of 2.73–70.8 nmol l^{–1} d^{–1}, with this process becoming progressively more important toward the core of the OMZ. Thus, N₂O turnover should be quite rapid.

Coastal waters off Peru exhibit some of the highest concentrations of N₂O observed in the ocean at or close to sea surface. Based on measurements made 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 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 N₂O concentration in subsurface waters (175–195 nM) are from shallow, high-NO₂[–] (most probably suboxic) waters (see Fig. 1B in Codispoti et al., 1992). This is very similar to observations over the western Indian shelf and would support the view that such high concentrations represent transient accumulation of N₂O during denitrification at shallow depths. As in the case of the Arabian Sea, the high surface concentrations feed large efflux of N₂O to the atmosphere (12.7–30.7 μmol m^{–2} d^{–1} – Fariás et al., 2009a). It may be noted that negative sea-to-air fluxes, implying net N₂O flux into the ocean, have also been reported from the region (Table 2b) (Pierotti and Rasmussen, 1980). Codispoti et al. (1992) computed the total annual emission from their area of observations (250 000 km²) to be 0.16 Tg N₂O. This is much smaller than the total annual emission (0.8 Tg N₂O) estimated by Pierotti and Rasmussen (1980) for the entire O₂-deficient region of the ETSP. However, the latter is prob-

ably an overestimate in view of the systematically high N₂O concentrations measured by these authors in the atmosphere for which corrections have been made in the data included in Table 2b.

Off Central Chile (30°–40° S)

Regular monitoring of physical and biogeochemical conditions at the above-mentioned COPAS time series site included N₂O since its inception in 2002. The time series records show the recurrence of hypoxia/suboxia in the water column every summer (Fig. 7b). The onset of O₂ 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 (Fariás et al., 2004).

As anticipated, N₂O 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 N₂O 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 N₂O production (Fig. 7c) occur during periods of most intense O₂ deficiency (Fig. 7b) and accumulation of NO₂[–] in bottom waters (Fig. 7d) (Cornejo et al., 2007). The association of high N₂O values with varying O₂ levels points 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 (δ¹³C-POC) showed that chemolithoautotrophs and specifically aerobic ammonium oxidizers are active in the region, especially during the upwelling period, facilitating elevated production of N₂O (Fariás et al., 2009b).

The onset of hypoxic/suboxic conditions affects the sediment-water exchange of dissolved nitrogen species (Fariás and Cornejo, 2007). Conditions in bottom water are influenced by benthic organic remineralization, which consumes O₂ as well as other electron acceptors such as NO₃[–]. Benthic fluxes of NO₃[–] (2.62–5.08 mmol m^{–2} d^{–1}) and N₂O (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), N₂O efflux off central Chile exhibits marked seasonality (Cornejo et al., 2007). The upwelling period is characterized by N₂O emission from the ocean to the atmosphere (up to 195 μmol m^{–2} d^{–1}), while low, even negative values of sea-to-air flux (to –9.8 μmol m^{–2} d^{–1}) are obtained for the non-upwelling period (May–July), with the annual average exceeding 10 μmol m^{–2} d^{–1} (Cornejo et al., 2007; L. Fariás, unpublished). The zonal distribution of N₂O flux across

Table 2a. Concentrations and sea-to-air fluxes of CH₄ from major hypoxic/suboxic/anoxic zones.

Region	Surface/mixed layer concentration (nM)	Maximum subsurface (depth) concentration (nM)	Sea to air flux ($\mu\text{mol m}^{-2} \text{d}^{-1}$)	References
Normoxic Open Ocean	Slightly supersaturated with respect to atm. CH ₄ (e.g. ~2 nM in the tropics)	Maximum at the base of the mixed layer (e.g. ~3 nM in the tropics)	Variable, but mean <0.5 $\mu\text{mol m}^{-2} \text{d}^{-1}$	Bates et al. (1996); Reeburgh (2007); Rhee et al. (2009)
Deep Hypoxic/Suboxic Systems				
Eastern Tropical North Pacific	1.8–4.1	6.5 (140 m)	Not given (N.G.)	Burke et al. (1983)
	2.3–4	28 (350 m)	0.77–3	Sansone et al. (2001)
Eastern Tropical South Pacific	2.1–4	12.8 (150 m)	~0–4.3	Kelley and Jeffrey (2002)
Arabian Sea	<2–5.3	10.1 (35 m), 8.2 (200 m)	~0–13.9	Owens et al. (1991); Jayakumar et al. (2001); Naqvi et al. (2005)
Bay of Bengal (>10° N)	1.7–4.1	6.5 (75 m)	–0.9–4.7	Berner et al. (2003)
Naturally Hypoxic Shelf Systems (including deeper basins)				
Eastern Tropical North Pacific				
Mexican margin (open)	3.2–5.7	46 (340 m)	0.5–2.7	Sansone et al. (2004)
Mexican margin (Gulf of California basins)	3–4.5	25–78 (400–530 m)	0.5–5.9	Sansone et al. (2004)
California Borderland basins	2.9–10.5 ^a	~50 (50 m, 550 m) ^a	0.1–>147 ^a	Ward (1992); Cynar and Yayanos (1992, 1993); Kessler et al. (2008)
Eastern Tropical South Pacific (Off central Chile)	3.1–29.2	79.9 (90 m)	0.05–59.5	Farias et al. (2009b); L. Farias, unpublished
Eastern Tropical North Atlantic (Off Mauritania)	2–5	N.G.	0.5–0.8	Kock et al. (2008)
Eastern Tropical South Atlantic (off Namibia)	2.2–2870	5160 (18 m) 200–2000 (Benthic Boundary Layer)	3–752 N.G.	Scranton and Farrington (1977) Monteiro et al. (2006) Brüchert et al. (2009)
Eastern Arabian Sea (Indian shelf)	2.6–47.6	44 (24 m)	0.58–63.7	Jayakumar (1999); G. Narvenkar, unpublished
Northern Bay of Bengal	3.2–38.3	12.9 (78 m)	0.22–24.9	Berner et al. (2003)
Anthropogenically-produced Coastal Hypoxic Systems				
Gulf of Mexico	<3–750	708 (15 m)	N.G.	Kelley (2003)
Changjiang (Yangtze River) Estuary and East China Sea	2.8–49	85.9 (5 m)	0.02–440	Zhang et al. (2008b)
Land-locked Anoxic Basins				
Baltic Sea				
Eckernförde Bay (Pockmark site)	2–106	441 (25 m)	–0.4–413	Bussmann and Suess (1998)
Eckernförde Bay (Boknis Eck Time Series Station)	7–42	235 (20 m)	6–15	Bange et al. (2010)
Kiel Fjord	80–1000	8000 (10 m)	N.G.	Schmaljohann (1996)
Baltic Proper	4–695	N.G.	10–1200	Bange et al. (1994)
Baltic Proper	4–22	403 (depth N.G.)	N.G.	Dzyuban et al. (1999)
Mariager Fjord	500–900	30 000 (30 m)	240–4500	Fenchel et al. (1995)
Black Sea				
Northwest, largely shelf	4–255	200 (50 m)	32–470	Amouroux et al. (2002)
Deep basin	10	13 050 (1650 m)	26.6–50	Amouroux et al. (2002); Reeburgh et al. (1991); Kessler et al. (2006a)
Cariaco Basin	~2	16 780 (1370 m)	0.23	Ward et al. (1987); Kessler et al. (2006b)
Saanich Inlet	23.4–50	1609 (175 m)	2.3–57	Bullister et al. (1982); Lilley et al. (1982); Ward et al. (1989)

^a Except stations located very close to coast sampled by Cynar and Yayanos (1992, 1993) where surface and subsurface values reached up to ~1200 nM and 1400 nM, respectively, with sea-to-air fluxes as high as 4350 $\mu\text{mol m}^{-2} \text{d}^{-1}$.

Table 2b. Concentrations and sea-to-air fluxes of N₂O from major hypoxic/suboxic/anoxic zones.

Region	Surface/mixed layer concentration (nM)	Maximum subsurface (depth) concentration (nM)	Sea to air flux ($\mu\text{mol m}^{-2} \text{d}^{-1}$)	References
Normoxic Open Ocean	Slightly supersaturated with respect to atm. N ₂ O (e.g. ~5–6 nM in the tropics)	Coincides with the oxygen minimum (e.g. ~30 nM at ~500 m in the equatorial Atlantic)	Variable but mean <1 $\mu\text{mol m}^{-2} \text{d}^{-1}$	Butler et al. (1989); Nevison et al. (1995); Rhee et al. (2009)
Deep Hypoxic/Suboxic Systems				
Eastern Tropical North Pacific	4.9–11.1	86.9 (65 m)	–5.6–15.9	Cohen and Gordon (1978); Pierotti and Rasmussen (1980); Yamagishi et al. (1997)
Gulf of California	12.5	84.4 (705 m)	N.G.	Yamagishi et al. (1997)
Eastern Tropical South Pacific (Off Peru and northern Chile)	6.1–37.8	86 (30 m)	–1.1–30.7	Pierotti and Rasmussen (1980); Farias et al. (2009b)
Arabian Sea	5.2–16.7	85.6 (800 m)	~0–470	Naqvi et al. (2005)
Bay of Bengal	4.95–7.6	79.6 (205 m)	0.6	Naqvi et al. (1994)
Naturally Hypoxic Shelf Systems				
Eastern Tropical South Pacific				
Off Peru	< 11.4–172.7	195.5	~39	Codispoti et al. (1992)
Off central Chile	6.7–58.9	245 (30 m)	–9.8–195	Cornejo et al. (2007)
	5.1–30.1	206 (40 m)	–7.7–42.9	Farias et al. (2009a); L. Farias, unpublished
Arabian Sea				
Omani shelf	9.7–24.7	48.8 (50 m)	N.G.	S. W. A. Naqvi, unpublished
Indian shelf	5.3–436	765 (19 m)	–1.2–3243	Naqvi et al. (2006b)
Western Bay of Bengal	4.9–12.0	42.0 (120 m)	–0.1–10.7	Naqvi et al. (1994)
Anthropogenically-produced Coastal Hypoxic Systems				
Gulf of Mexico	5–7	47	0.6–11.7	Walker et al. (2010)
Changjiang (Yangtze River) Estuary and East China Sea	5.8–37.2	62.6 (20 m)	–0.7–97.5	Zhang et al. (2008b)
Chesapeake Bay	6.6–9.8	Highest value at the surface	N.G.	Elkins et al. (1978)
Tokyo Bay	8.8–139	Highest value at the surface	1.51–153	Hashimoto et al. (1999)
Land-locked Anoxic Basins				
Baltic Sea				
Baltic Proper	14–20	1523 (110 m)	5–11	Rönnner (1983)
Gotland Basin	13	63 (90 m)	N.G.	Brettar and Rheinheimer (1991)
Baltic Proper	10–12	31 (90 m)	N.G.	Walter et al. (2006)
Eckernförde Bay (Boknis Eck Time Series Station)	10–17	19 (25 m)	N.G.	Schweiger (2006)
Black Sea				
Northwest shelf	6.5–8	N.G.	1.6–4.4	Amouroux et al. (2002)
Deep basin	7.5–10.2	14.4 (70 m)	3.1–5.2	Amouroux et al. (2002); Butler and Elkins (1991); Westley et al. (2006)
Cariaco Basin	4.4–5.5	11.7 (200–225 m)	N.G.	Hashimoto et al. (1983)
Saanich Inlet	11.3–11.6	20.4 (110 m)	N.G.	Cohen (1978)

eastern South Pacific along latitude 32.5° S (Charpentier et al., 2010) also shows a very large increase (by a factor of 30) in N₂O emissions within the coastal zone 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 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), discussed in detail in Sect. 5. A comprehensive overview of CH₄ and N₂O measurements in European coastal waters is given in Bange (2006b). Within the context of this article we focus on the (rare) studies of CH₄ and N₂O during hypoxic/anoxic events in shallow waters.

4.5.1 Methane

Accumulation of CH₄ (up to 8 μM) in the Kiel Harbour has been observed during stagnation periods when the water column turns anoxic toward the end of the summer (Schmaljohann, 1996). Since June 2006, CH₄ measurements have been performed at the Boknis Eck Time Series Station (Eckernförde Bay, Southwestern Baltic Sea) on a monthly basis (Bange et al., 2010). Methane concentrations in the bottom layer (20–25 m) at Boknis Eck were up to 235 nM in October 2007; however, maximum CH₄ concentrations were not concurrent with hypoxic/anoxic events which usually occur in September/October. This apparent decoupling of hypoxic/anoxic events and the variability of CH₄ concentrations in the water column was explained by CH₄ release from sediments which occurred with a time lag of about one month after the sedimentation of organic material originating from phytoplankton blooms. Hypoxic/anoxic events seemed to have only a modulating effect on the accumulation of CH₄ in the water column (Bange et al., 2010). Considerable CH₄ release from sediments takes place despite the fact that CH₄ diffusion into the water column can be efficiently prevented by anaerobic CH₄ oxidation in the sediments of Eckernförde Bay (Treude et al., 2005).

4.5.2 Nitrous oxide

At the Boknis Eck Time Series Station (Eckernförde Bay, SW Baltic Sea), N₂O has been measured on a monthly basis since July 2005 (Schweiger, 2006; Bergmann, 2009). Figure 8 shows the temporal N₂O variability during the hypoxic/anoxic event from September to October 2005. It is obvious that a pronounced N₂O accumulation occurred after the water column was ventilated in November 2005. An increase of the N₂O concentrations from 1–10 nM (in October 2005) to 16–20 nM (in November 2005) was recorded (Fig. 8).

Concurrent measurements of hydroxylamine (NH₂OH), the first intermediate of NH₄⁺ oxidation during nitrification, showed that maximum concentrations of NH₂OH were observable in November 2005 as well. This led to the conclusion that both N₂O and NH₂OH 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 O₂ commonly occurs in near-bottom coastal waters of Southeast Asia including the delta of the Mekong River (63–94 μM O₂) and the Pearl River Estuary (31–63 μM O₂) (Yin et al., 2004). Similar conditions have also been reported recently from the East China Sea (ECS) off the Changjiang Estuary (e.g. Fig. 9e), with bottom-water O₂ concentrations of 63–94 μM occurring over an area of 15 000 km² in August 1999 (Li et al., 2002).

The Changjiang empties into the ECS with a mean water discharge of 928×10⁹ m³ a⁻¹ and total suspended matter (TSM) load of 0.35×10⁹ t a⁻¹, of which 70–80% occurs during the flood season (May–October) (Yang et al., 2002). The freshwater plume from the Changjiang disperses at the surface in the ECS (Fig. 9d) and at its peak in summer covers an area of ~85 000 km². 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. 9a) 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 CH₄ 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, CH₄ 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 CH₄ concentrations

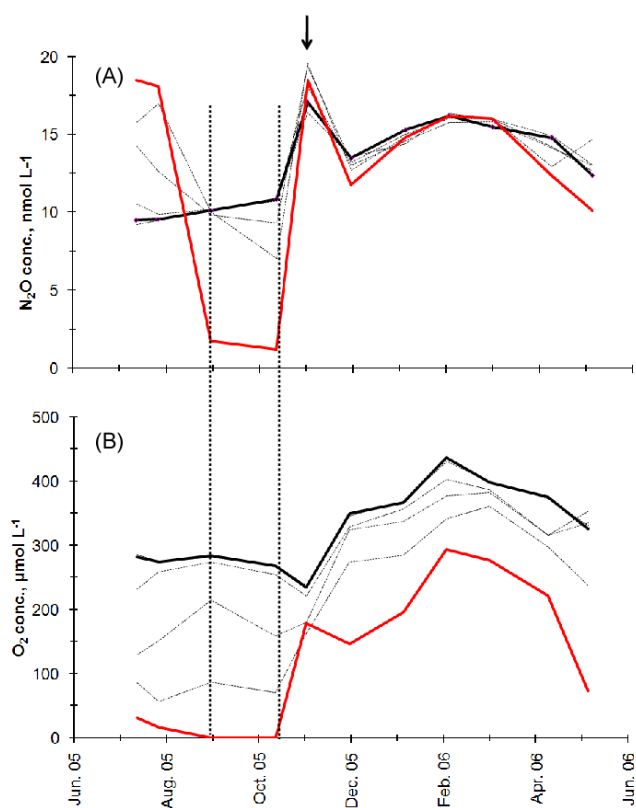


Fig. 8. Variability of N₂O (A) and O₂ (B) at Boknis Eck time series station in the western Baltic Sea from July 2005 to May 2006. The hypoxic/anoxic event is marked by vertical dashed lines. Concentrations at 1 m and 25 m are highlighted with bold black and red lines respectively. The thin dashed lines 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).

declining with depth down to 1000 m (Zhang et al., 2004). Over the ECS shelf, the upwelled Kuroshio subsurface waters have relatively low O₂ (125–156 μM) with lower CH₄ concentrations than in near-bottom waters over the inner shelf. Thus, in the coastal waters of the ECS that are affected by eutrophication, an increase of CH₄ saturation occurs in the water column (Fig. 9a), thereby sustaining a higher sea-to-air flux of CH₄ (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. 9e) every summer (from June to September), with the lowest O₂ levels recorded in near-bottom waters being 16–31 μM between 20–50 m isobaths in the late summer of 2003. Also, waters with O₂ 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 CH₄ 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 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 CH₄ 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 CH₄ 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 O₂ at a rate of 30–70 mmol m⁻² d⁻¹, while CH₄ efflux from the sediments has been quantified as 1.7–2.2 μmol m⁻² d⁻¹; CH₄ and O₂ 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. 9b) and air-sea exchange of N₂O in the coastal region off the Changjiang Estuary and further offshore in the ECS are regulated by the prevailing hydrographic conditions (Fig. 9c–e) and nitrogen cycling. For instance, the upwelled water of the Kuroshio at the shelf break is characterized by relatively low O₂ with slightly higher N₂O 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. 9b; 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 the Changjiang during the summer season (Fig. 9c, d). Concentrations of N₂O in the hypoxic layer (O₂ < 63 μM – Fig. 9e) 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 N₂O concentrations in the near-shore and open shelf regions are similar, hovering around 10 nM. Off the Changjiang Estuary, ΔN₂O is positively correlated with AOU but in a non-linear way; there also exist positive correlations between N₂O on the one hand and NH₄⁺ and NO₃⁻ on the other suggesting that N₂O is mainly produced through nitrification (Zhang et al., 2008b).

The sea-to-air flux of N₂O in the region of coastal hypoxia off the Changjiang Estuary is up to 50–100 μmol m⁻² d⁻¹, an order of magnitude higher than the values for the shelf mixed water of the ECS (<10 μmol m⁻² d⁻¹), Kuroshio waters (<5 μmol m⁻² d⁻¹) (Zhang et al., 2008b), and also the

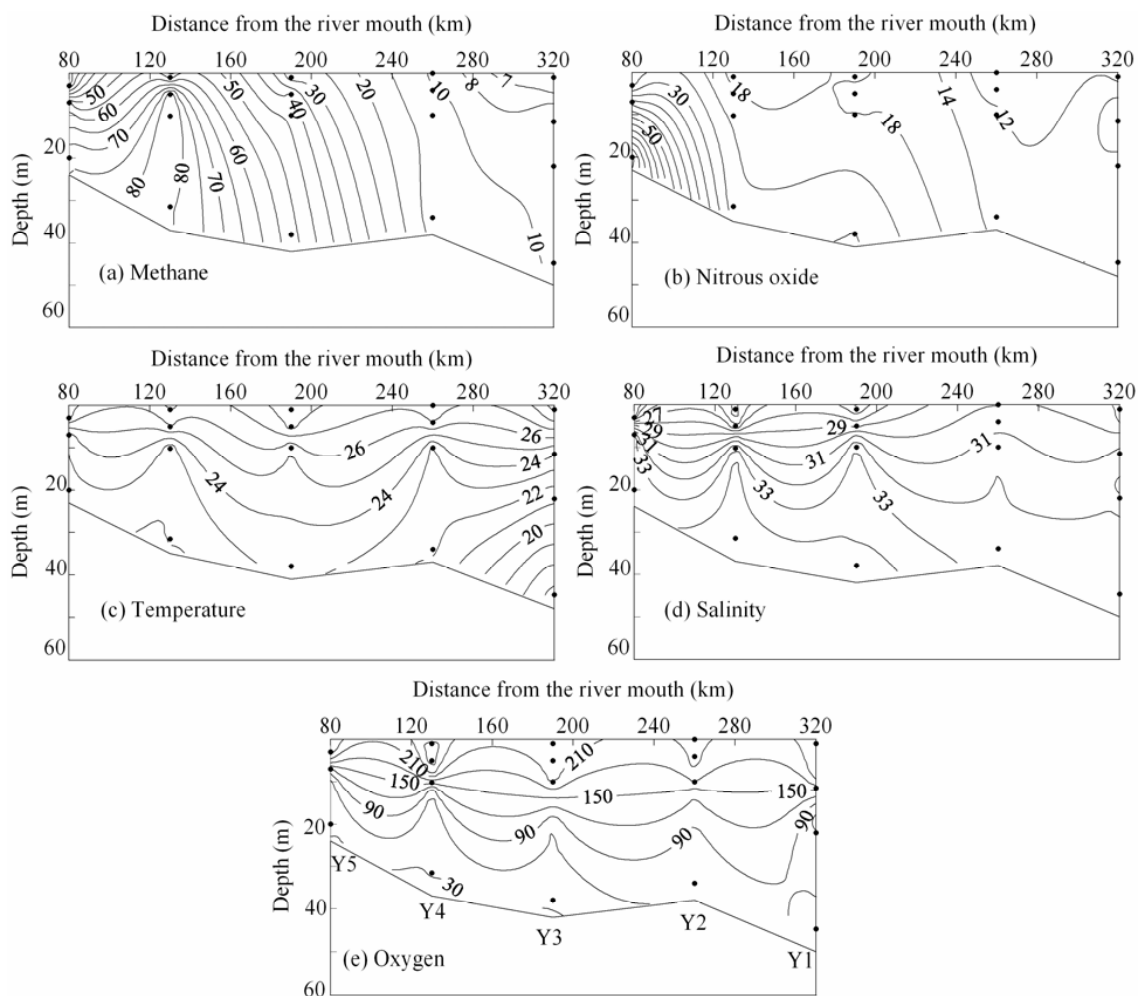


Fig. 9. Distribution of hydrographic and chemical properties in the East China Sea from a station outside Changjiang Estuary (Y5) to the Korea Strait (Y1) in September 2003: (a) CH₄ (nM), (b) N₂O (nM), (c) temperature (°C), (d) salinity, and (e) dissolved O₂ (µM). Modified from Zhang et al. (2008b).

Changjiang water ($20 \mu\text{mol m}^{-2} \text{d}^{-1}$, 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 CH₄ and N₂O 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 ($580 \text{ km}^3 \text{ a}^{-1}$ – 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 its 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 CH₄ cycling (Brooks et al., 1981).

4.7.1 Methane

Supersaturation of surface waters of the Gulf of Mexico with respect to atmospheric CH₄ 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 CH₄ (originating from anoxic degradation of organic matter and from seeps or gas hydrates) from shelf sediments, lateral dispersal of CH₄-rich layers, and in situ production (Brooks et al., 1981). An extensive data set on

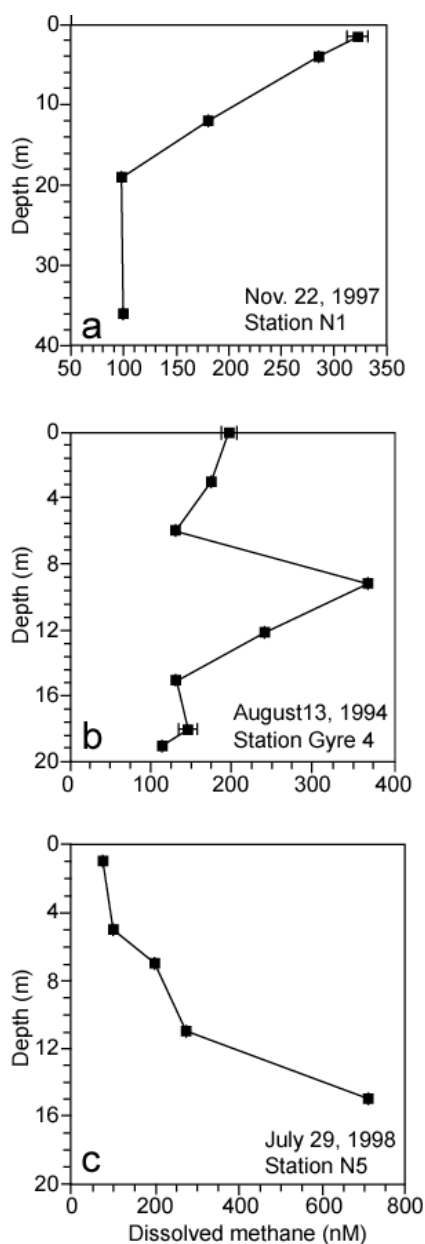


Fig. 10. Vertical profiles of CH₄ at three stations located over the shelf in the region affected by the Mississippi plume in the Gulf of Mexico. Modified from Kelley (2003).

CH₄ 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 CH₄ concentrations, some even matching those observed off Namibia. These high values persist during all seasons, but tend to be more elevated during summer. Although surface waters had lower salinity (down to 20) as compared to bottom waters (~35), peak values were not always associated with the Mississippi plume with CH₄ maxima occurring at the surface (Fig. 10a), at mid-depth (within the pycnocline,

Fig. 10b) or close to the bottom (Fig. 10c). Kelley did not present O₂ data, if they were collected, but bottom-water hypoxia might have been present during the summer samplings (e.g. in case of Fig. 10b and c). The observed accumulation of CH₄ 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 CH₄ 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 CH₄ from the sediments coupled with low O₂ content of the bottom water may also be important contributors to the greatly elevated CH₄ 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-CH₄ water and/or the loss of CH₄ from the surface layer through air-sea exchange.

4.7.2 Nitrous oxide

The first data set on N₂O distribution and atmospheric emission from the Gulf of Mexico has just been made available by Walker et al. (2010). Their observations in August 2008 were interrupted by Tropical Storm Edouard, allowing them to quantify the emission pulse caused by storm-driven vertical mixing. Although hypoxic conditions prevailed in near bottom waters prior to the storm, the O₂ concentrations were not low enough (suboxic) for denitrification to occur. N₂O concentrations ranged from 5 to 30 nM with the highest values observed at mid-depths or close to the bottom. These concentrations and the computed sea-to-air fluxes (0.6–6.9 μmol m⁻² d⁻¹) were higher than those in the Caribbean and western Tropical Atlantic. The storm led to generally higher values of N₂O (7–47 nM) as well as an increase in the N₂O emission rate (1.2–11.7 μmol m⁻² d⁻¹). While the higher surface concentrations were obviously due to entrainment of N₂O from the hypoxic bottom water, the enhanced production through nitrification was attributed to reoxygenation of the water column and redistribution of organic nitrogen.

As in other areas (e.g. Rhee et al., 2009), inputs of N₂O by river water to the Gulf of Mexico do not seem to be important as evident from the data of Fox et al. (1987) from the Mississippi Estuary. These data, collected during a period of low flow (October 1983), show close-to-saturation concentrations above a salinity of 20, and an almost conservative mixing behaviour in fresher waters with ~200% saturation occurring at 0 salinity.

4.8 Tokyo Bay

A study of N₂O 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 O₂ depletion that prevailed in bottom waters during summer; instead their origin was a sewage treatment plant that generated a large amount of N₂O (~0.1 Gg N a⁻¹). In fact, the N₂O concentration decreased with depth as the bottom waters were reducing and had lost almost all NO₃⁻. Anomalously high NO₂⁻ or N₂O 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. Once oxic conditions were restored throughout the water column in October, both NO₃⁻ and N₂O increased in bottom water but still remained well below the surface values.

4.9 Chesapeake Bay

The Chesapeake Bay, the largest estuary in the United States and one of the largest in the world, has been experiencing seasonal hypoxia for several decades (e.g. Hagy et al., 2004; Kemp et al., 2009). Elkins et al. (1978) investigated vertical N₂O distribution in the deeper parts of the estuary during a period of peak hypoxia (in July 1977). As in case of the Tokyo Bay, the suboxic sub-thermocline waters having very low NO₃⁻ and NO₂⁻ but high NH₄⁺ concentrations were also depleted with N₂O. Surface waters were moderately supersaturated during stable conditions but became slightly undersaturated following a mixing event.

5 Methane and nitrous oxide in enclosed anoxic basins

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 a circulation where 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 (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 CH₄ in sulphidic waters (e.g. up to ~13 μM in the Black Sea (Fig. 11), 17 μM in the Cariaco Basin (Fig. 11) and 1.6 μM in the Saanich Inlet) (Bullister et al., 1982; Kessler et al., 2006a, b; Reeburgh, 2007; Ward et al., 1989). The source of CH₄ in these basins is believed to be sedimentary (Reeburgh, 2007). Kessler et al. (2005) measured ¹⁴C in CH₄ in the Cariaco Basin and reported that

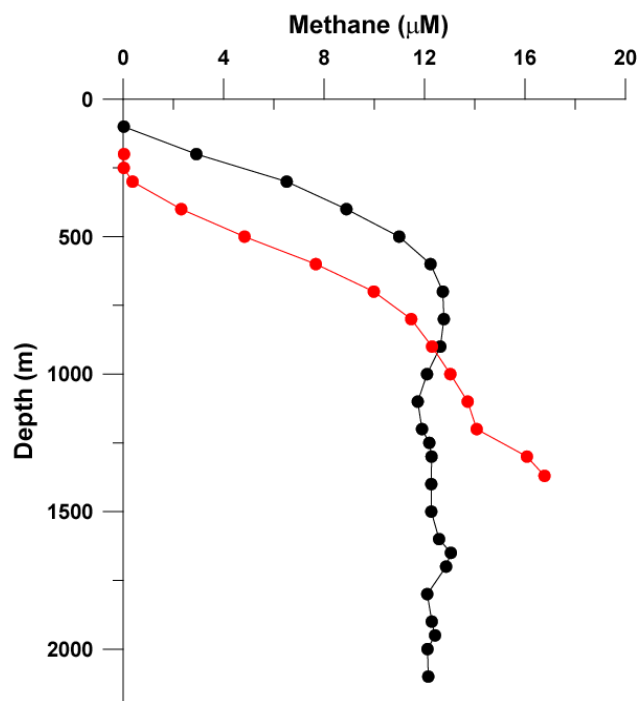


Fig. 11. Typical vertical profiles of CH₄ in the Black Sea (black symbols and curve) and the Cariaco Basin (red symbols and curve). Data are from Kessler et al. (2005, 2006a, b).

essentially all of the CH₄ in deep waters must be from fossil sources, in spite of earlier estimates of biogenic production (Reeburgh, 1976). However, deep-water CH₄ 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 CH₄ 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; M. I. Scranton, unpublished), while in the Black Sea, where there are several seeps, high surface CH₄ can be observed (e.g. 294% saturation observed over a 90 m deep seep – Schmale et al., 2005).

5.2 Nitrous oxide

Vertical distribution of N₂O in anoxic basins is significantly different from that observed in the open-ocean suboxic zones. As expected, the sulphidic layer is devoid of N₂O, a feature first noticed by Cohen (1978) in the Saanich Inlet (Fig. 12), 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 N₂O 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 interface (Fig. 12). The highest concentration

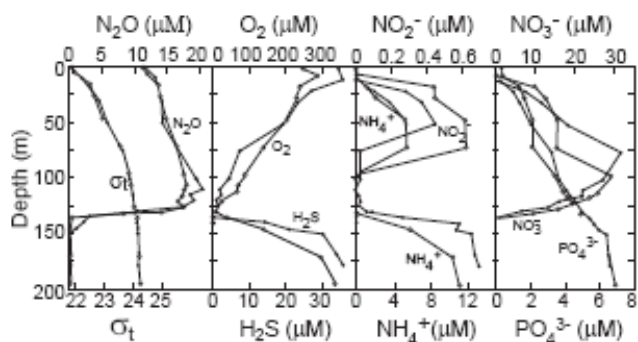


Fig. 12. Vertical profiles of (a) density (σ_t) and N₂O; (b) O₂ and H₂S; (c) NH₄⁺ and NO₂⁻; and (d) PO₄³⁻ and NO₃⁻ at two stations in the Saanich Inlet. Reproduced with permission from Cohen (1978).

is much lower than observed in open-ocean O₂-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 N₂O concentrations in these basins are even lower (<12 nM and <15 nM, respectively).

The spatial and temporal patterns of N₂O variability observed in the Baltic Sea are quite puzzling. The first N₂O 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 fortuitously observed a dramatic change in N₂O 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 N₂O concentration from 1523 nM to 0 nM within 24 h.

In a more recent study, Walter et al. (2006) investigated water-column distributions of N₂O 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 O₂ 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 N₂O concentrations were <2 nM. The peak N₂O 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 O₂-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 N₂O accumulation in the water column. However, the accumulated N₂O was not immediately released to the atmosphere because of the presence of a permanent halocline.

Westley et al. (2007) provided data on isotopic composition of N₂O from the Black Sea that are very intriguing in that the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ exhibited opposite trends, contrary to observations in other O₂-deficient systems (e.g. Kim and Craig, 1990; Yoshinari et al., 1997; Naqvi et al., 1998). Within the N₂O-maximum layer at the lower oxycline, there was a slight depletion of ¹⁵N and slight enrichment of ¹⁸O 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 $\delta^{15}\text{N}$ fell to a minimum of -10.8‰ (the lowest ever reported from seawater) whereas $\delta^{18}\text{O}$ rose to a maximum of 67.0‰. The isotomeric data revealed a ¹⁵N site preference maximum that coincided with the $\delta^{18}\text{O}$ maximum. These results were interpreted to infer that both production of N₂O through oxidation of NH₄⁺ diffusing upward from the anoxic layer and consumption of N₂O through denitrification were occurring within the suboxic layer, producing both depletion and enrichment of the heavier isotopes, respectively. In case of ¹⁵N, depletion due to production probably overwhelmed enrichment due to consumption. However, Westley et al. did not rule out other processes such as anammox influencing N₂O cycling in the Black Sea. The above results underscore our incomplete understanding of the mechanisms of N₂O production and consumption in systems approaching and reaching complete anoxia.

6 Discussion

It is believed that most of the CH₄ accumulating in bottom waters is derived from anoxic sediments through diffusion and bubble ebullition. The O₂ content/redox state of bottom waters is expected to affect sedimentary CH₄ production, its escape to the overlying water column, and its oxidative loss in the upper sedimentary column and in water itself. Therefore, one may expect an enhancement of CH₄ concentrations in O₂-depleted bottom waters. However, O₂-depletion does not seem to be a necessary and sufficient condition for dissolved CH₄ accumulation in the water column. High CH₄ concentrations (hundreds of nanomolar) are sometimes found in well-oxygenated waters overlying organic-rich sediments, as in the well known case of the Cape Lookout Bight (Martens and Klump, 1980) where hypoxic conditions do not develop at any time of the year (Kelley, 2003). Conversely, the world's largest naturally-formed coastal hypoxic zone over the Indian shelf does not exhibit large CH₄ build-up. Nevertheless, as discussed above and summarized in Table 2a, most O₂-deficient systems from which CH₄ data are available accumulate CH₄ to varying degrees. This includes the three major open-ocean OMZs in the ETNP (Fig. 5c), ETSP and the Arabian Sea where significantly elevated concentrations of CH₄ are found within the suboxic layer (Burke et al., 1983; Sansone et al., 2004; Kelley and Jeffrey, 2002; Jayakumar et al., 2001). The CH₄ maximum

coincides with the intermediate nepheloid layer, a ubiquitous feature of suboxic zones (Burke et al., 1983; Jayakumar et al., 2001), and so in addition to the continental margin origin (Sansone et al., 2001), in situ production within reducing microenvironments is another plausible mechanism of its formation.

Maximal CH₄ build-up (to micromolar levels) in seawater occurs in truly anoxic (sulphidic) enclosed basins. In the most prominent of such basins, having the highest CH₄ concentrations (the Black Sea and the Cariaco Basin), ¹⁴CH₄ measurements have established that fossil CH₄ released at the seafloor dominates over that produced through sediment diagenesis as a source to the water column (Kessler et al., 2005, 2006a). Thus, while anoxic conditions probably facilitate CH₄ preservation, their contribution to its production may be less important. Methane concentrations also increase, to a smaller extent (tens of nanomolar levels), in some silled basins overlain by hypoxic waters (e.g. the Gulf of California basins), but not in others (e.g. the California Borderland basins). It may be noted that occasional CH₄ maxima observed in the Santa Barbara Basin and Santa Monica Basin, reaching up to 50 nM (Kessler et al., 2008), most probably originate from lateral supply of CH₄ seeping from the seafloor. The above differences among hypoxic silled basins may be attributed to differences in sedimentary CH₄ supply and the residence time of water below the sill.

Along the open coasts too, bottom-water CH₄ content responds variously to changes in the ambient O₂ concentration. Over the Namibian shelf, where CH₄ content is inversely related to O₂ concentration in the bottom water (Monteiro et al., 2006), anoxic (sulphidic) waters have the highest CH₄ concentrations reaching up to ~5 μM. The increase in concentration (to ~40–50 nM) over the western Indian shelf during periods of anoxia is two orders of magnitude smaller. As pointed out earlier, the switch-over from hypoxic to suboxic conditions has little effect on bottom-water CH₄ content in this region, possibly because of deeper sulphate-CH₄ transition in the sediment arising mainly from its low organic carbon content. In the hypoxic zone of the Gulf of Mexico, on the other hand, much higher (hundreds of nanomolar) CH₄ levels are maintained despite a less intense hypoxia, evidently due to much larger supply from the sediments. According to Bange et al. (2010), CH₄ production in sediments of the Eckernförde Bay (Baltic Sea) and its supply to bottom waters is primarily linked to phytoplankton blooms with some (~1 month) time lag, and hypoxia exerts only a secondary modulating effect. This may also apply to most other areas. This implies that in areas where CH₄ accumulation and bottom water O₂ deficiency appear to be closely linked (see Figs. 2 and 7), the two may be driven by the same phenomenon – local high primary production – rather than having a direct cause-effect relationship. The other extreme case, as exemplified by the Indian shelf, appears to be where the O₂ deficiency is primarily due to low O₂ content of source waters and the local primary production is not that high such

that bottom-water CH₄ and O₂ are, to a large extent, decoupled.

In hypoxic coastal areas located close to river mouths (e.g. Gulf of Mexico, East China Sea, eastern Arabian Sea and northern Bay of Bengal), CH₄ concentrations are also enhanced by riverine inputs. Another complexity arises from in situ production of CH₄ in the water column itself, for which there is considerable circumstantial evidence (Scranton and Brewer, 1977; Scranton and Farrington, 1977; Karl and Tilbrook, 1994; 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 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).

Estimates of sea-to-air flux densities from major hypoxic/suboxic/anoxic zones are summarized in Table 2a for CH₄ and Table 2b for N₂O. An effort has been made in Tables 3a and b, respectively for the two gases, to quantify total emissions from all areas of the oceans affected by O₂ deficiency using representative figures for various types of systems. However, while considering these estimates the following caveats must be kept in mind:

1. The estimated fluxes given in Table 2 were obtained using different models of the air-sea gas exchange.
2. Only diffusive fluxes are considered, ignoring emissions via bubble ebullition. The latter are significant in the case of CH₄, even exceeding diffusive fluxes in some shallow regions. For instance, Martens and Klump (1980) measured a large flux of gaseous CH₄ (averaging 16.8 mmol m⁻² (low tide)⁻¹) in summer out of the sediments of the Cape Lookout Bight. Approximately 85% of the rising bubbles escaped dissolution in this shallow setting, resulting in an annually-averaged emission of ~12 mmol CH₄ m⁻² d⁻¹ to the atmosphere. This flux is 5–7 times the combined inputs of CH₄ to the water column through diffusion from sediments and dissolution of bubbles. Assuming that ~1% of the global continental shelf area shallower than 10 m (1.4 × 10⁶ km²) has a bubble ebullition CH₄ flux density comparable to that in the Cape Lookout Bight, an upper limit on the total flux from such systems could be placed at ~1 Tg a⁻¹. Not much is known about the bubble ebullition flux from coastal hypoxic zones except that such flux should be important over the Namibian shelf (Brüchert et al., 2006, 2008), and also expected to be so in the Gulf of Mexico, given the high CH₄ concentration in the water column (e.g. Fig. 10c).

Table 3a. Total CH₄ emissions from various types of marine O₂-deficient systems.

Region	Area (km ²)	Flux density (μmol m ⁻² d ⁻¹)	Total flux (Tg CH ₄ a ⁻¹)
Open-ocean hypoxic zones	29.3 × 10 ⁶ ^a	1.6 ^b –2.2 ^c	0.27–0.38
Naturally-formed continental-margin hypoxic zones	1.1 × 10 ⁶ ^d	2.8 ^e –11.2 ^f	0.02–0.07
Athropogenically-formed hypoxic zones			
Persistent	88 000 ^h	21–36 ⁱ	0.01–0.02
Periodic/Seasonal ^g	138 000 ^h	21–36 ⁱ	0.008–0.015
Enclosed anoxic basins	0.83 × 10 ⁶	10–50 ^j	0.05–0.24
Total	31.5 × 10 ⁶		0.36–0.72

^a Paulmier and Ruiz-Pino (2009); ^b Open Arabian Sea – Naqvi et al. (2005); ^c Open ETNP – Sansone et al. (2001); ^d Helly and Levin (2004); ^e Mexican continental margin – Sansone et al. (2004); ^f Western Indian shelf – Jayakumar (1999); ^g Assumed for 6 months; ^h Diaz and Rosenberg (2008); ⁱ East China Sea – Zhang et al. (2008); ^j Chosen from various references in Table 2a.

Table 3b. Total N₂O emissions from various types of marine O₂-deficient systems.

Region	Area (km ²)	Flux density (μmol m ⁻² d ⁻¹)	Total flux (Tg N ₂ O a ⁻¹)
Open-ocean hypoxic zones	29.3 × 10 ⁶	2.7 ^a –4.5 ^b	1.27–2.12
Naturally-formed continental-margin hypoxic zones	1.1 × 10 ⁶	10–50 ^c	0.18–0.88
Athropogenically-formed hypoxic zones			
Persistent	88 000	3.3 ^d –17.1 ^e	0.004–0.024
Periodic/Seasonal ^f	138 000	3.3 ^d –17.1 ^e	0.003–0.019
Enclosed anoxic basins	0.83 × 10 ⁶	1.6–5.2 ^g	0.02–0.07
Total	31.5 × 10 ⁶		1.48–3.11

^a ETNP – Cohen and Gordon (1978); ^b Open Arabian Sea – Naqvi and Noronha (1991); ^c Chosen from various references in Table 2b; ^d Gulf of Mexico – Walker et al. (2010); ^e East China Sea – Zhang et al. (2008); ^f Assumed for 6 months; ^g Black Sea – Amouroux et al. (2002).

The extent of CH₄ supply to the atmosphere by bubbles rising from seeps, clathrates and mud volcanoes at deeper seafloor in areas such as the Black Sea and Gulf of Mexico has become a subject of considerable interest in recent years. McGinnis et al. (2006) quantified dissolution of CH₄ from such bubbles from a combination of modelling and acoustic observations and concluded that most of the CH₄ carried by bubbles venting from sites deeper than 100 m in the Black Sea does not reach the atmosphere. However, a more recent study by Solomon et al. (2009) involving direct submersible sampling of water around hydrocarbon plumes in the Gulf of Mexico has challenged this view. These authors showed that bubble dissolution could be inhibited by bubble size, upwelling flows and the presence of surfactants. This

together with slow oxidation seems to ensure significant transport of CH₄ from deeper seep sites to the surface layer and atmosphere. Thus, the issue is yet to be fully settled.

3. Ranges of various flux density estimates provided in Table 2 are quite large. As a consequence, selection of representative values for various types of systems (Table 3) leads to large uncertainty. In most cases, we have chosen reasonable reported maximal and minimal mean flux density values so as to keep the ranges as narrow as possible. Another uncertainty pertains to the estimates of areas covered by various types of systems, especially those formed as a result of human activities (eutrophication). These estimates, from Diaz and Rosenberg (2008), are available for only one-quarter of

all anthropogenically-formed hypoxic zones. The remaining three-quarters of such systems are smaller in size, and hence would not add very much to the total area. Moreover, this may be compensated to some extent by the fact that a few systems falling under the anthropogenic group are also included elsewhere (e.g. the Danish coastal waters are counted again under enclosed anoxic basins). For these reasons, estimates of fluxes provided in Table 3 should be treated as crude first approximations, enabling an evaluation of their relative importance.

Despite modest sea-to-air flux density (Table 2a) the open-ocean OMZs are the largest source of CH₄ diffusing to the atmosphere from the sea surface among all hypoxic regions listed in Table 3a. This term is also the best constrained as estimates of the flux density for all other groups are much more variable. Among the naturally-formed hypoxic zones of the continental margins, the Namibian shelf is arguably the most important CH₄ emitter. However, atmospheric fluxes of CH₄ from this region are very poorly quantified. To give an idea of the potential importance of this region, an area of ~100 000 km² of the suboxic zone (Kuypers et al., 2005) and an assumed average flux density of 200 μmol m⁻² d⁻¹ (toward the lower range of estimate in Table 2a for this region) would yield a total annual flux of ~0.12 Tg CH₄. This very crude calculation shows that the total CH₄ efflux from natural hypoxic zones of the continental margins may be comparable to that from open-ocean OMZs. The enclosed anoxic basins occupy slightly smaller area but are distinguished by the highest CH₄ concentrations. However, as the CH₄-rich anoxic, subsurface waters are well isolated from the atmosphere, the total emission from these systems is not very large. Finally, at present there is a dearth of data on CH₄ emissions from anthropogenically-formed coastal hypoxic zones. If the estimates from the region off the Changjiang mouth in the East China Sea are taken to be representative of this group, as has been done in Table 3a, emissions from this group will be negligible. However, it should be noted that, given the high surface concentrations reported by Kelley (2003) from the Gulf of Mexico hypoxic zone, CH₄ flux density for this region, and in some other similar systems, may be substantially higher than that reported for the East China Sea. All marine areas affected by hypoxia put together emit up to ~1 Tg CH₄ annually. While constituting a significant fraction of global oceanic CH₄ emission (in fact, it is comparable to the total CH₄ efflux from global ocean, 0.6–1.2 Tg a⁻¹, reported by Rhee et al., 2010), it still represents merely 0.2% of all inputs of CH₄ to the atmosphere (Reeburgh, 2007).

In view of the lack of evidence for a primary control of bottom-water hypoxia on sedimentary CH₄ production, as well as low estimated emissions of CH₄ from the anthropogenically-formed coastal hypoxic zones, it is highly unlikely that an intensification or expansion of such zones

will have a large impact on global oceanic emissions of CH₄ to the atmosphere. A more important factor favouring methanogenesis in coastal sediments could be the potential increase in productivity due to eutrophication or intensification of coastal upwelling due to global warming (Bakun, 1990). At present, it is difficult to quantify or predict such changes. Nevertheless, it would be reasonable to conclude that unless CH₄ 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 CH₄ budget, is unlikely to change.

The available information on N₂O distribution and computed fluxes across the air-sea interface is summarized in Table 2b. Nitrous oxide cycling differs from that of CH₄ in three respects: (1) N₂O is mainly produced in the water column; (2) its production by all known mechanisms is enhanced at low O₂ concentrations; and (3) it has no sink in oxygenated waters. As stated earlier, N₂O does get reduced to N₂ within the cores of suboxic zones, but the peripheries of these zones provide most suitable conditions for its production. Consequently, O₂-deficient aquatic systems are generally net producers of N₂O (e.g. Codispoti et al., 1992). However, the extent to which the loss of O₂ promotes N₂O production varies from one system to another (Table 2b) for reasons that are still not clear. The response of N₂O to deoxygenation is non-linear. The “normal” behaviour is that N₂O values peak at tens of nanomolar levels just before the environment turns reducing (e.g. Fig. 5a). Such enhancement of the N₂O yield, recorded in both (largely) natural (e.g. off Oman) and (largely) anthropogenic (e.g. off China) hypoxic/suboxic systems (Table 2a), is most likely due to nitrifier denitrification (oxidation of NH₄⁺ to NO₂⁻ followed by the reduction of NO₂⁻ to gaseous nitrogen species by autotrophic nitrifiers) (Yamagishi et al., 2007). Deviations from this behaviour, where N₂O concentrations climb up to hundreds of nanomolar levels (Table 2b), have been observed in three naturally-formed coastal suboxic environments (off India, Peru and Chile). We predict similar abnormally high N₂O concentrations off Namibia as well. The most important common feature of these systems is the extension of OMZ to very shallow depths. The most probable way by which N₂O accumulates in very high concentrations in such settings is a more rapid reduction of NO₂⁻/NO to N₂O as compared to its own reduction to N₂ by denitrifiers. This requires an inhibition of the activity of N₂O 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 N₂O cycling is not well understood and difficult to predict. This is, for example, illustrated by data from the Boknis Eck time series station (see Fig. 8) where N₂O only peaks when the system is shifting from suboxic/anoxic (reducing) to oxic conditions which is in contrast to the “normal” behaviour discussed above.

Behaviour of N₂O in anoxic basins is quite puzzling. While its reduction to N₂ expectedly accounts for near-zero levels in sulphidic waters, the build-up below the oxygenated mixed layer is well below expectation (e.g. Fig. 12), except for the aforementioned event in the Baltic where N₂O concentration shot up to a world-record high level of ~1.5 μM (Table 2). One explanation for this could be that vertical transition from oxic to suboxic and then anoxic conditions in these basins is rapid, but then such is also the case over the western Indian shelf where, as stated above, abnormally high N₂O concentrations often occur in close proximity to sulphidic waters. It would seem that shallow but unstable suboxia maintains high levels of N₂O over the Indian shelf (Codispoti, 2010), whereas the nitrogen cycle is more often in a steady state in enclosed anoxic basins. Another important factor that probably contributes to the lower N₂O levels in the anoxic basins is the low concentrations of secondary NO₂⁻ (e.g. Fig. 12).

Among the anthropogenically-formed coastal hypoxic zones, N₂O data are available from the East China Sea, Gulf of Mexico, Chesapeake Bay and Tokyo Bay. These systems show different trends that can be related to different redox conditions prevailing at the time of observations. That is, bottom waters were hypoxic in the East China Sea and Gulf of Mexico, and nearly-anoxic (having very low NO₃⁻+NO₂⁻ and high NH₄⁺) in the other two areas. Accordingly, there was moderate accumulation of N₂O at the first two sites. The Chesapeake Bay and Tokyo Bay exhibited a trend similar to enclosed anoxic basins, except for high surface values in the Tokyo Bay that clearly originated from a sewage treatment plant, as discussed earlier. Overall, the data gathered so far from the anthropogenically-formed coastal hypoxic zones have not shown the kind of N₂O build-up that distinguishes naturally-formed, upwelling-related coastal suboxic zones, but a number of other anthropogenically-formed systems still remain to be investigated.

Estimates of sea-to-air flux density generally reflect the trends of N₂O variability in the water column (Table 2b). The highest flux densities are computed for the naturally-formed hypoxic zones of the continental margins followed by open-ocean OMZs, anthropogenically-formed coastal hypoxic zones and enclosed anoxic zones in decreasing order. As in case of CH₄, total efflux of N₂O is the largest from open-ocean OMZs. This estimate also happens to be the most robust. Estimates for the naturally-formed coastal hypoxic zones are much more uncertain; even for the data-rich hypoxic zone over the Indian shelf, they vary from 0.05 to 0.38 Tg N₂O a⁻¹ (Naqvi et al., 2006b). The upper limit of emissions estimated by us for this group (0.88 Tg N₂O a⁻¹) compares well with the reported global emission of 0.86 Tg N₂O-N a⁻¹ from the estuaries and continental shelves by Seitzinger and Kroeze (1998). Our computations show that the anthropogenically-formed coastal hypoxic zones and enclosed basins presently do not contribute very significantly

to the total marine N₂O emission to the atmosphere. Our estimate for N₂O emission from all hypoxic/suboxic/anoxic zones (1.48–3.11 Tg N₂O a⁻¹) represents 16–33% of the total oceanic N₂O source to the atmosphere, lower than 50% considered by Codispoti (2010). However, it is higher than the estimate for efflux of N₂O from the global oceans (0.9–1.7 Tg N₂O-N a⁻¹) provided by Rhee et al. (2009). Considering such a substantial contribution from areas experiencing O₂ deficiency in the water column to the global marine N₂O emission, and of the latter to the atmospheric N₂O budget, and also taking into account the sensitivity of N₂O cycling in aquatic systems to minor changes in the ambient O₂ concentration in the very low range, one may conclude that any major alterations in O₂ distribution in coastal as well as off-shore waters are certain to have a large impact on the N₂O budget. However, 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.

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