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Nitrous oxide and methane in marine systems.

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CHAPTER 6

Summary and concluding remarks

The present increase in the atmospheric concentrations of nitrous oxide (N_2O) and methane (CH_4) is of concern since together these gases account for about 20% of the enhanced global warming due to human activities. In addition N_2O is also involved in the destruction of the stratospheric ozone layer. In order to understand the causes responsible for the atmospheric increases, all sources and sinks of N_2O and CH_4 need to be quantified. The aim of this thesis is to contribute to a better assessment of the marine environment as a source of atmospheric N_2O and CH_4 , thereby focusing on the role of estuaries, coastal waters, and upwelling regions. Research concentrated on: (1) the quantification of the distribution of N_2O and CH_4 in contrasting marine environments; (2) the assessment of the resulting gas emissions to the atmosphere; and (3) the identification of the microbial processes underlying the emissions. The main findings of this research are summarised below, and are followed by concluding remarks.

N_2O in the northwest Indian Ocean

A study on N_2O was carried out in the Somali Basin, northwest Indian Ocean, during the height of the southwest monsoon season. The strong monsoon winds, inducing upwelling of cold subsurface water off the Somalian coast, had a major impact on the biogeochemistry of the region. The vertical N_2O distribution over the water column of the Somali Basin exhibited two maxima: (1) a sharp subsurface maximum at about 150 m depth, characterised by N_2O supersaturations of up to ~1000% with respect to atmospheric solubility, and (2) a broad deep water maximum around 800 m depth, characterised by saturations up to ~800%. Below the wind mixed layer, N_2O was always negatively correlated with oxygen and positively with nitrate, indicating that N_2O was produced by nitrification. The average yield of N_2O production, relative to nitrate production, was approximately 0.17%. At oxygen concentrations below 15-20 $\mu\text{mol dm}^{-3}$, the N_2O yield during nitrification increased to about 0.35%. Denitrification was of minor importance, since the oxygen concentration in the Somali Basin never dropped below approximately 10 $\mu\text{mol dm}^{-3}$.

The N_2O saturation in the surface waters was inversely correlated with temperature, indicating that monsoon-driven upwelling of cold N_2O -rich water controlled the saturation degree of N_2O in surface waters. Outside the upwelling region, surface waters were only slightly supersaturated with respect to the atmosphere, whereas the N_2O saturation in freshly upwelled waters amounted to 330%. The strong monsoon wind driving the upwelling, also induced strong vertical mixing and effective air-sea gas exchange. As a consequence, N_2O emissions into the atmosphere reached values as high as 260 to 500 $\mu\text{mol m}^{-2} \text{d}^{-1}$, which is nearly 3 orders of magnitude above the globally mean oceanic N_2O flux. By using temperature as an indicator of upwelling, satellite images of sea surface temperature were applied to extrapolate the observed N_2O emissions in space and time. It was estimated that during the two months of most intense upwelling, the Somalian upwelling region may account for 2.5 - 5% of the global marine N_2O emission, from an area of less than 0.011% of the world ocean.

N_2O in the Scheldt estuary

Dissolved N_2O was studied in the Scheldt estuary in relation to the distributions of nitrification activity, oxygen, NH_4^+ , and NO_3^- , along the estuarine salinity gradient. The Scheldt estuary is characterised by elevated loadings of organic matter and nutrients, which induce intense mineralisation, and associated depletion of oxygen in the upper estuary. Dissolved N_2O was always supersaturated with respect to the atmosphere. Saturation ranged from about 3000% in the oxygen-poor waters at low salinities to slight supersaturation at the mouth of the estuary. N_2O production largely originated from nitrification in the water column. The location and intensity of nitrification was controlled by: (1) the oxygen gradient along the estuary, ranging from strong undersaturation at low salinities to complete saturation at sea, and (2) the NH_4^+ concentration of the river water entering the estuary. In the oxygen-poor waters at low salinities, the highest nitrification activity was about 6 $\mu\text{mol N dm}^{-3} \text{h}^{-1}$. The N_2O yield, associated with nitrification, varied spatially and seasonally. Between 0.1 and 0.4% of the oxidised NH_4^+ was converted to N_2O , rather than to NO_3^- . These yields are almost similar to the values observed in the Indian Ocean, as discussed before. A comparison with a data set from 1978, reported in literature, indicated that the main locus of N_2O production has shifted upstream during the last decades, in response to the gradually decreasing eutrophication and increasing oxygen concentrations in the estuary. Due to the residence time of about two months, nearly all N_2O was lost to the atmosphere within the estuary rather than being transported to the open sea. The average N_2O flux per unit area amounted to about 75 $\mu\text{mol m}^{-2} \text{d}^{-1}$, which is comparable to the fluxes in the Somalian upwelling region, but larger than values reported for most other estuaries.

The mean annual emission from the Scheldt estuary to the atmosphere was estimated to be 2.8×10^8 g. Extrapolation to the global scale indicated that the world-wide estuarine emission may be as large as 1.5 Tg yr^{-1} , corresponding to about 25% of the present estimates of the global marine N_2O source.

CH₄ in the Rhine estuary

Concentrations of CH_4 were measured in the Rhine estuary, its lower tributaries, and in its plume off the Dutch coast during 4 seasons. Surface waters were always supersaturated with CH_4 relative to the atmospheric concentration, along the entire transect from river to the coastal sea. Highest CH_4 concentrations ($0.45 - 0.85 \mu\text{mol dm}^{-3}$) were measured in the low salinity region of the estuary ($S = 1-4$), corresponding to 140-330 times supersaturation, which is high compared to other estuaries. Only about 30% of the CH_4 in the estuary was supplied by its major tributaries, whereas the remaining 70% was produced *in situ*, likely by the estuarine sediments. The *in situ* production in the estuary was positively related to temperature, suggesting that CH_4 originated from a microbial source.

The emission of CH_4 from the estuary to the atmosphere ($6 - 12 \text{ kmol d}^{-1}$) was about one order of magnitude lower than the CH_4 export to the coastal zone of the North Sea ($46 - 111 \text{ kmol d}^{-1}$). In the coastal zone, the estuarine water mass was transported northward by the residual current in a coastal plume extending 25 km offshore. In this plume, the distribution pattern of CH_4 followed the freshwater fraction, with contours parallel to the shoreline. Coastal CH_4 concentrations ranged from 250 nmol dm^{-3} (~100 times supersaturated) near the mouth of the Rhine estuary, down to 3 nmol dm^{-3} (slight supersaturation) outside the plume of the Rhine. The atmospheric loss in the plume of the Rhine ($183 - 288 \text{ kmol d}^{-1}$) was 3 to 4 times higher than the CH_4 exported by the estuary. Consequently, most of the coastal CH_4 was not supplied by the Rhine estuary, but rather by the coastal sediments. Per unit area, the calculated CH_4 supply by coastal sediments is 2 orders of magnitude lower than the CH_4 supply by estuarine sediments. Extrapolation of the CH_4 emission from the Rhine estuary to the global scale suggests that the world-wide estuarine CH_4 emission amounts to $0.4 - 1.4 \text{ Tg CH}_4 \text{ yr}^{-1}$. Although this emission corresponds to about 10% of the total marine CH_4 source, it contributes little to the global CH_4 budget.

Comparison of air-sea CH₄ fluxes derived by two methods

On a research platform off the Dutch coast, air-sea exchange of CH_4 was simultaneously quantified by two different methods. According to the first method,

fluxes were calculated from the measured concentration difference across the air-sea interface, multiplied with a transfer velocity derived from windspeed on the basis of an empirical relationship. This method underlies all present estimates of marine trace gas emissions. According to the second method, the gradient technique, fluxes were derived from the product of the turbulent exchange coefficient in the atmosphere and the vertical CH₄ gradient in the air above the sea surface. Fluxes derived by the gradient method were on average 6 times larger than fluxes based on measured air-sea concentration differences and estimated transfer velocities. This discrepancy, well-known from similar studies on CO₂, cannot be explained by experimental errors, nor by local variability in CH₄ concentrations. More simultaneous measurements by both methods are required to resolve this issue.

CONCLUDING REMARKS

Fluxes and extrapolations

All studies described in this thesis confirm the hypothesis that a relatively large proportion of the global marine emission originates from estuaries, coastal waters, and upwelling regions, although the relative importance of the sources differs for N₂O and CH₄.

Estuaries were estimated to contribute about 25% to the total marine N₂O source, and about 10% to the total marine CH₄ source. However, estuaries are a much more important factor in the global N₂O budget than in the global CH₄ budget, since they account for about 6% of the total N₂O source, whereas their contribution to the total CH₄ source is only about 0.2%, due to the overwhelming importance of terrestrial sources.

The study on N₂O in the Somalian upwelling region suggests that the role of upwelling regions as sources of atmospheric N₂O may still be underestimated. Bange et al. (1994) reported that upwelling regions contribute about 3% to the global marine N₂O emission. Given our estimate that the Somalian upwelling region alone may account for 2.5 - 5% of the global marine N₂O emission during the two months of most intense upwelling, it is likely that the estimated emissions from upwelling regions need upward revision. This conclusion is supported by the limited data from other upwelling regions (e.g. Law and Owens, 1991; Codispoti et al., 1993). Existing estimates of N₂O emissions from wind driven upwelling regions have been derived by combining *in situ* N₂O saturations with annual mean wind speeds. This approach may result in underestimation of the N₂O emission, since upwelling of N₂O-rich water is *coupled* to high wind speed in these areas. Therefore future research in upwelling regions should

focus on the height of the upwelling season, when the combined occurrence of high gas transfer velocities and rapid resupply of N_2O from subsurface layers sustains huge N_2O emissions to the atmosphere. Finally, satellite images of sea surface temperature, allowing extrapolation of fluxes in space and time, can be an important tool to improve estimates of the emission from upwelling regions.

Factors controlling gas production

This thesis indicates that dissolved oxygen is a key parameter controlling the location, the rate, and the efficiency of the microbial processes responsible for the production of N_2O and CH_4 . In addition, production of N_2O and CH_4 was shown to be positively related to the availability of organic carbon and nutrients.

Nitrification in the water column was the dominant source of N_2O production in both the Somali Basin and the Scheldt estuary, since these contrasting environments were characterised by the same range of oxygen concentrations. The N_2O yield during nitrification in both systems was almost equal, with highest N_2O yields coinciding with lowest oxygen concentrations. In addition, N_2O production in the Scheldt was related to the availability of NH_4^+ , supporting the hypothesis of Firestone and Davidson (1989) that N_2O production increases with increasing availability of N-compounds.

The study on CH_4 in the Rhine estuary indicated that CH_4 production was largely concentrated in the sediments, as was expected from the strict anoxic conditions required for CH_4 production. It was argued that the abundant availability of organic matter in the estuarine sediments induced CH_4 production rates that were two orders of magnitude higher than CH_4 production in sandy coastal sediments. Nevertheless, the CH_4 emission from the coastal plume of the Rhine was much higher than the CH_4 emission from the estuary itself, because of its larger aerial coverage. Consequently, future research in estuaries should explicitly include studies in the coastal plumes.

Finally, this thesis showed that different marine systems require different analytical approaches. In the open ocean, mostly characterised by slight supersaturation of both N_2O and CH_4 , it is vital to optimise the accuracy of the analytical-computational procedures, since a small bias in absolute concentrations can induce huge errors in the calculated fluxes. In contrast, highly dynamic systems, like estuaries and upwelling regions, require sampling with high resolution and fast analytical equipment, to cover the large spatial and temporal variation in concentrations, which may span more than two orders of magnitude.