



Small-scale methane and nitrous oxide measurements across the Black Sea chemocline

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The Black Sea is the largest anoxic water body of the world and a potential source of methane emission from bubbling or diffusive surface flux. We have measured methane concentrations across the chemocline to investigate the amount of methane reaching the surface and also to estimate the amount of methane oxidized anaerobically compared to the amount oxidized aerobically. Additionally we measured nitrous oxide concentrations to see, if it can be used as a tracer for nitrification and denitrification.

For this we measured methane and nitrous oxide concentrations and the stable isotope compositions across the chemocline of the Central and Eastern Black Sea. Nitrous oxide concentrations are close to the atmospheric equilibrium concentrations and vary from 78 - 140% and 55 - 121 % saturation for Station 1 and Station 2 respectively. Shortly before N_2O disappears in the anoxic zone concentrations rise slightly, suggesting a source of nitrous oxide. The origin of this source is not known. Overall, the Black Sea seems to be a sink for nitrous oxide, as there is a flux towards the anoxic zone.

Methane concentrations start to decline from approximately $12 \mu\text{mol}\cdot\text{l}^{-1}$ below the chemocline to about $10 \text{ nmol}\cdot\text{l}^{-1}$, which is very close to the atmospheric equilibrium concentration. Simultaneously the carbon isotope composition of methane starts to rise from around -60 ‰ , VPDB to values between -30 to -40 ‰ , above the chemocline.

In the oxic surface water there is again an increase in methane concentrations to over 100 nM. This methane is thought to be produced by zooplankton, in anaerobic sites of sea snow, is transported laterally from shallower sediments or vertically by a plume. The isotopic signal ranges from -50 to -60 ‰ , and supports both hypotheses, as these

values can be the result of methane diffusing from Black Sea sediments, as well as from biogenic methane. Increased methane concentrations (around $400 \text{ nmol}\cdot\text{l}^{-1}$) in the samples from the surface waters of the Eastern Black Sea are thought to be the result of contamination of oil transport from the port in Gelendjik through the Bosphorus. This is based on the relatively high carbon isotope signal of -40% , and the high amounts of higher hydrocarbons that were found in these samples.

Our data suggests that only a very small fraction ($< 1 \%$) of methane dissolved in the deep waters of the Black Sea crosses the chemocline and most of it is consumed by anaerobic methane oxidation. Methane existing in the surface water is from other sources and most likely the result of internal production or pollution.