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Vertical pathways of methane in the Black Sea

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Introduction

Methane, after carbon dioxide, is the second most important greenhouse gas in the atmosphere. Methane has 21 times the global warming potential as the same mass of carbon dioxide (St. Louse et al. 2000). Methane concentrations have doubled from 850 ppb to approximately 1750 ppb over the last 150 years (Cicerone and Oremland 1998). This concentration, however, would be even much higher if the huge methane pools that are stored in ocean and lake sediments would be released to the atmosphere. Current research has therefore focused on the atmospheric methane contribution from gas hydrates and seeps, a phenomenon that has been overlooked some 20-30 years ago (Kvenvolden 1988).

In the Black Sea, measurements were performed on R/V *Professor Vodyanitsky* during the two CRIMEA (EC project EVK-2-CT-2002-00162) cruises, May - June 2003 and 2004. In the north western Black Sea, hundreds of active gas seeps were detected along the shelf and slope of the Crimea Peninsula at water depths between 35 and 800 m. Active gas seeps down to 2100 m water column were also detected. This portion of the CRIMEA project focuses on the fate of the methane resulting from both shallow and deep seeps. Results are presented detailing methane transport in the Black Sea due to 1) bubble transport, 2) methane-induced bubble plumes 3) vertical turbulent diffusion and 4) methane oxidation rates. These transport mechanisms allow us to estimate the conditions and means by which methane released from seeps reaches the surface.

Results

In dispersed seeps, which typically occur at the shallow sites, methane is released intermittently as bubbles. Vertical transport is therefore by bubble dissolution in the water column, or gaseous release to the atmosphere. Using a bubble model which tracks an individual bubble traveling through the water column, we are able to determine the amount of methane transported to the surface as a function of depth and initial bubble diameter. The equations of state for gas account for the non-ideal behavior of gaseous mixtures at high pressure. The model, which includes argon, nitrogen, oxygen, methane and CO_2, was verified using air bubbles in shallow conditions (McGinnis and Little 2002) as well as for argon and methane bubbles released deep in the ocean (430 – 820 m; Rehder et al. 2001) with excellent results. The model demonstrates that large bubbles from shallow depths are needed to transport a significant quantity of methane to the atmosphere (99.8% methane dissolution from an 8 mm bubble released at 100 m depth). However, when seeps are strong and release high volumes of gas then a plume may be generated that advectively transports bubbles higher in the water column

One potential plume site is at an active mud volcano located at approximately 1850 m depth where gas bubbles could be seen on the echosounder up to 1000 m water depth, i.e. a bubble flare could be followed 850 m through the water column. The single bubble model predicts that an improbably large (30 mm) diameter methane bubble would be required to rise this high in the water column. Therefore, for this rise height, either a bubble plume must be present, the bubbles have different properties in the hydrate stability field, or both. A bubble-plume model was developed to examine the conditions under which such a large plume could exist. An important aspect of the deep-water bubble plume model is that it accounts for the variable buoyancy flux due to 1) isothermal expansion of water; 2) the density contributions of dissolved methane, salt and thermal fluxes; and 3) changes in bubble size due to stripping or dissolution. Using the boundary conditions (temperature, methane, salinity and CO_2) obtained near the deep water seep and a source diameter of 100 m, the bubble size (10 mm) and gaseous methane flux (50 mol s^{-1} or 0.025 Tg yr^{-1}) were adjusted to reach approximately 900 m.

Methane dissolved in shallow waters may also diffuse to the atmosphere. Therefore, the vertical diffusivity is estimated from the over 70 temperature microstructure profiles obtained during the two cruises. The profiles were processed by fitting to the theoretical Batchelor spectrum to estimate the dissipation rate of turbulent kinetic energy. The data are then used to calculate the turbulent diffusivity of constituents through the thermocline and halocline. The results indicate that turbulence within the stratified water column is very weak. Using the average measured vertical diffusivity

of K_z = 1×10^{-6} m^2 s^{-1} and a concentration gradient of 0.3 nM/m, the upward flux of dissolved methane in the surface 50 meters yields a basin-wide vertical flux in the surface layer of 70 Mg yr^{-1} (1.6×10^{-4} g m^{-2} yr^{-1}).

As the diffusivity is low, it is likely that a large portion of the dissolved methane in the shallow water is oxidized before reaching the atmosphere. Background methane concentrations vary around 11 μM in the deep water; however concentrations up to 16 μM have been detected in the area of active seeps. At a shallow seep site, the methane increase was even more pronounced with concentrations approximately 4 times higher compared to an off-seep site. Given the high methane oxidation rates, and the corresponding high turnover of, on average, approximately 2 - 3 years, it is likely that a substantial portion of the surface-water methane is oxidized, preventing large fluxes from reaching the atmosphere. This is in agreement with the very low methane flux estimate (70 Mg yr^{-1}).

Conclusions

It is estimated that the Black Sea contains a total of 96 Tg of methane (Reeburgh et al. 1991). The methane oxidation rate is calculated to be 30 Tg yr^{-1}, yielding a methane residence time of approximately 3 years, a relatively short period of time. Converting the methane oxidation rate to an equivalent areal carbon production yields 50 g C m^{-2} yr^{-1}, which is in good agreement to the 240 g C m^{-2} yr^{-1} of primary production reported by Sorokin (2002). Experience tells us that approximate 10% of primary productivity results in a net system carbon production (i.e. 24 g C m^{-2} yr^{-1}), therefore approximately 50% of the methane would be from methanogenesis and 50% would be from geological sources, such as methane plumes.

Preliminary conclusions indicate that methane plumes from deep water sources, while perhaps strong (e.g. the estimated $\sim$0.025 Tg yr^{-1} estimated from the single, deep plume in this study), stop well below the surface. Depending on the initial bubble size, methane reaches the surface only in shallow sites ($<$ about 100 m), however, most is dissolved and subsequently oxidized in the water column. Plume formation, while less likely in shallower regions, will also increase the amount of methane which reaches the surface. However, the high oxidations rates and low diffusivities lead to surface flux estimates of less than 70 Mg yr^{-1}, concluding that the Black Sea is not a significant contributor of methane to the atmosphere.

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