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Upward flux of methane in the Black Sea: Does it reach the atmosphere?

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ABSTRACT: As methane has 21 times the global warming potential as the same mass of carbon dioxide, it is important to determine the physical processes which contribute to the upward flux to the atmosphere from methane-containing submarine seeps. The Black Sea's contribution to the global methane flux is a growing concern, it is important to properly understand the relevant transport mechanisms in the water column. Subsurface methane is released into the water column in the Black Sea from destabilizing methane hydrates and active seep areas. Vertical methane transport can occur due to bubble transport, methane-induced bubble plumes and turbulent diffusion. The combination of modeling and analysis reveals that advective methane transport to the surface from plumes and gas bubbles is very low, and only occurs in very shallow sites (<200 m). Furthermore, the low turbulent diffusion coefficient and the relatively high methane oxidation rates are important processes that hinder high methane contributions to the atmosphere.

1 INTRODUCTION

Methane, after carbon dioxide, is the second most important greenhouse gas in the atmosphere and has caused dramatic climate shifts in the past several million years (Dickens, 2000; Hinrichs et al., 2003). Methane has 21 times the global warming potential as the same mass of carbon dioxide (St. Louis et al., 2000). Anthropogenic inputs, such as rice paddies, livestock, and biomass combustion contribute the largest proportion to the atmospheric concentration (71%) (Reeburgh, 1996). Methane concentrations have in fact doubled from 850 ppb to currently approximately 1750 ppb over the last 150 years (Cicerone & Oremland, 1998). Natural sources, such as wetlands and termites, contribute, along with other small sources, approximately 29%. Recently, it has been suggested that up to 18% of the atmospheric methane is emitted from reservoirs (St. Louis et al., 2000).

Atmospheric methane concentrations, 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 methane contribution from gas hydrates, a phenomenon that has been overlooked some 20–30 years ago (Kvenvolden, 1988). Higher temperatures from global warming lead to the dissociation of methane hydrates and the subsequent release of methane to the water column. It is estimated that twice the amount of energy is stored in gas hydrates than in all combined coal, gas, and oil deposits (Kvenvolden, 1988). In this study, we estimate the vertical flux of methane in the Black Sea above gas seeps resulting from methane hydrate destabilization to determine how much, if any, methane reaches the atmosphere.

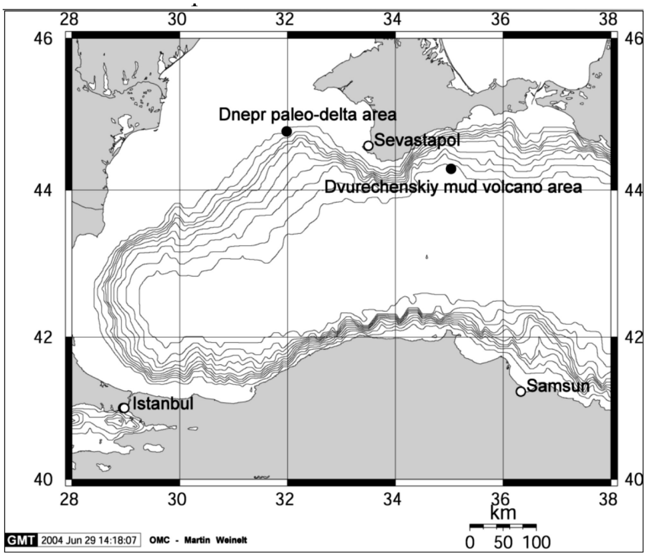

Figure 1. Black Sea study sites (map from OMC) for which methane release assessment was performed.

The Black Sea has a surface area of 423,000 km^2, a volume of 5.45×10^5 km^3 and a maximum depth of 2212 m, making it the largest anoxic water basin in the world (Ross & Degens, 1974). Originally a freshwater lake, the Black Sea became brackish when the Bosporus made a full connection to the Mediterranean waters about 7150 yr ago due to glacial activity (Ryan & Cita, 1977; Görür et al., 2001). Freshwater river inflow resulted in lower surface water salinity (17.5–18.5‰), whereas the deep water salinity is 22.3‰ (Murray, 1991). Due to the permanently stable stratification, anoxia developed in the hypolimnion ($\sim$4.7 km^3) over the past several thousands of years, with the aerobic surface waters separated by a chemocline of 100-200 m deep, depending on location (Sorokin, 2002).

In the north western Black Sea, hundreds of active gas seeps occur along the shelf and slope of the Crimea Peninsula at water depths between 35 and 800 m (Ivanov et al., 1991). Recently, active gas seeps down to 2100 m water column have been detected in the Dvurechenskii mud volcano area (Fig. 1) (44° 16′N, 34° 58′E, Bohrmann & Schenk, 2002). This portion of the CRIMEA project (EC project EVK-2-CT-2002-00162) focuses on the fate of the methane resulting from such seeps, i.e. physical transport and the microbial methane oxidation. To determine the physical processes which contribute to the upward flux from these seeps, it was necessary to combine various modeling and analysis techniques to understand these transport mechanisms in the water column. Results are presented detailing methane transport in the Black Sea due to (1) bubble transport, (2) methane-induced bubble plumes and (3) vertical turbulent diffusion. These transport mechanisms are then compared with the methane concentrations and oxidation rates, which allows us to estimate the conditions and means by which methane released from seeps reaches the surface.

2 METHODS AND LOCATIONS

Measurements were performed at the shallow (Dnepr paleo-delta area) as well as the deep (Dvurenchenskiy area) seep sites with R/V *Professor Vodyanitsky* during the two CRIMEA cruises, May–June 2003 and 2004 (Fig. 1). An active mud volcano was located at the Dvurenchenskiy site at approximately 1850 m depth where gas bubbles could be seen on the echosounder up to 1000 m water depth, i.e. a flare of bubbles could be followed 850 m through the water column. Therefore

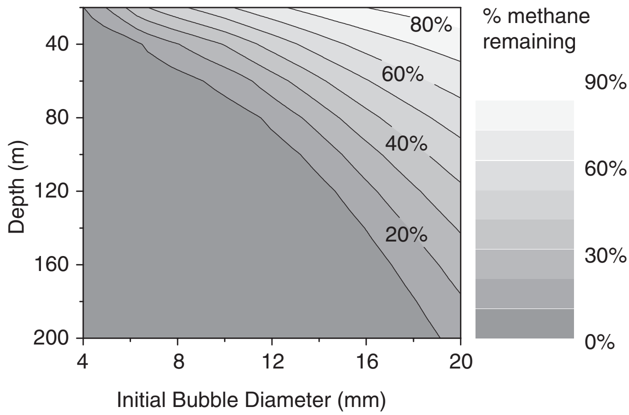

Figure 2. Model results: percent of methane reaching the surface from a 100% methane bubble.

temperature profiles where collected using both a Seabird SBE 25 CTD probe (Conductivity, Temperature and Depth, sampled at 25 Hz) and a modified Seabird SBE 9 CTD profiler equipped with fast response thermistors (sampled at 96 Hz) at both sites. Water samples were also collected to measure methane concentrations and methane oxygenation rates. These data are then used to look for the occurrence of plumes, and as boundary conditions for modelling of bubble plumes and turbulent transport.

3 RESULTS

3.1 *Bubble transport*

In dispersed seeps, which typically occur at the shallow sites, methane is released intermittently where the buoyancy introduced by bubbles is not sufficient to drive a plume. Vertical transport is therefore by bubble dissolution in the water column, or gaseous methane transport to the atmosphere. Using a bubble model which tracks an individual bubble traveling through the water column (McGinnis & Little, 2002), we are able to determine the amount of methane transported to the surface as a function of depth and bubble diameter (Fig. 2).

The equations of state for gas have been modified to account for non-ideal behavior of gaseous mixtures at high pressure. The model includes nitrogen, oxygen, methane and CO_2. As shown in Figure 1, a rather large bubble from a relatively shallow depth is needed to transport a significant quantity of methane to the atmosphere. However, bubbles, even if not reaching the atmosphere, will dissolve methane higher into the water column where it is more likely to diffuse to the atmosphere (Section 3.3). When seeps are strong and release high volumes of gas, or have a high heat flux, then a plume may be generated.

3.2 *Plume transport*

Plumes advectively transport dissolved methane as well as bubbles higher in the water column. CTD profiles obtained during the Spring 2003 cruise are used to look for evidence of these plumes. A technique, called the Thorpe scale analysis, is used to reorder the temperature profiles to give a corresponding smooth profile (Thorpe, 1977) (Fig. 3). This allows us to locate turbulent overturns and the associated small-scale temperature inversions. Figure 3 shows 30 m mixing lengths at around 950 meters depth, with the corresponding profile section shown on the right. Although not all of the CTD temperature profiles have been analyzed, such overturn lengths have not been observed in the off-seep site temperature profiles. These large overturns correspond to the same

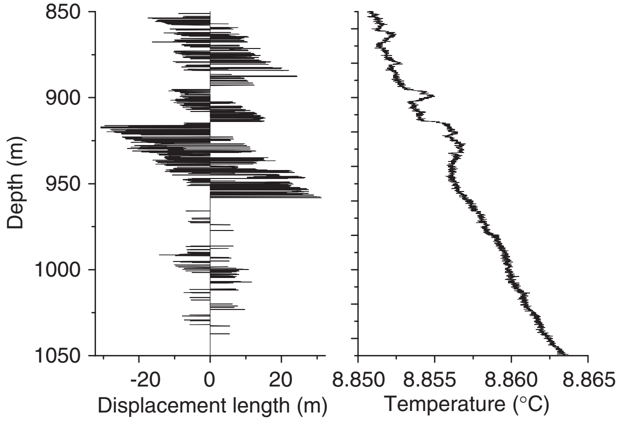

Figure 3. An example of a temperature profile near the deep seep and the corresponding Thorpe scale displacement.

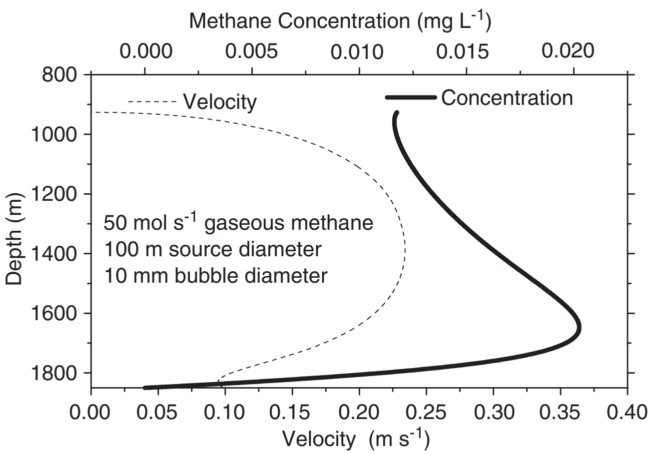

Figure 4. Preliminary plume model results showing plume velocity and in-plume methane concentration.

location as the previously discussed active mud volcano (Section 2) where gas bubbles could be seen on the echosounder up to 1000 m water depth. The energy represented by the overturns shown in Figure 3 is likely added by the plume at this location.

To determine if such a large plume could exist, a previously developed bubble-plume model was employed. The model is based on fundamental principles and is applicable to deep-water bubble plumes with some modifications. An important aspect of the model is that it accounts for the variable buoyancy flux due to (i) isothermal expansion of the rising plume water; (ii) the density contribution of dissolved methane and thermal fluxes, both of which also increase the buoyancy; and (iii) changes in bubble size. Appropriate plume modeling is important in that both the rising plume and gas bubbles are the key deep-water physical transport mechanisms for methane.

Figure 4 shows the preliminary bubble-plume model results using the boundary conditions (temperature, methane, salinity and CO_2) obtained near the deep water seep. Using a source diameter of 100 m, bubble size (10 mm) and gaseous methane flux (50 mol s^{-1} or 0.025 Tg yr^{-1}) were adjusted such that the plume reached approximately 900 m. Note the initial acceleration of the

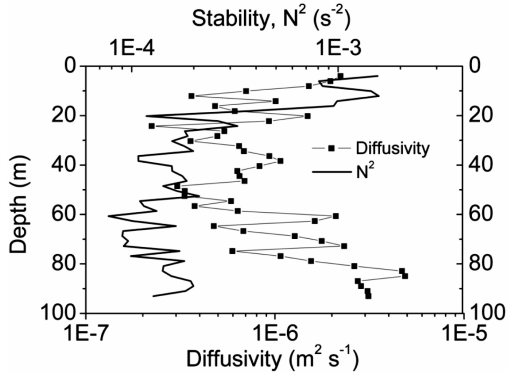

Figure 5. Diffusivity estimates and water column stability from microstructure profiles.

plume in the lower 200 m. Dissolved methane decreases water density, which increases the plume buoyancy. This effect stops when enough ambient water is entrained to dilute the high methane concentration in the plume.

3.3 *Vertical diffusion*

Methane bubbles and methane induced plumes, regardless of whether they reach the surface, enhance the upward vertical transport of methane, potentially leading to higher concentrations in the shallow waters and subsequent diffusion to the atmosphere. The vertical diffusivity is estimated from the 34 temperature microstructure profiles obtained in spring 2003. 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 (Fig. 5). The results indicate that turbulence within the stratified water column is very weak. From Figure 5, the vertical diffusivity in the surface water is $K_z = 1 \times 10^{-6}\ m^2\ s^{-1}$, the upward flux of dissolved methane into the surface 50 meters can then be calculated as

$$F_{CH_4} = A_z K_z \frac{\partial C_{CH_4}}{\partial z},$$

where A_z is the area of the Black Sea at 50 m, and the right-hand term is the methane concentration gradient. Using a concentration gradient of 0.3 nM m^{-1} yields a basin-wide vertical flux in the surface layer of 70 Mg yr^{-1} (1.6E−4 g m^{-2} yr^{-1}).

3.4 *Methane oxidation*

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. The Black Sea water column contains spatially varying amounts of methane, with concentrations in the oxic surface waters in the nano-molar range and concentrations in the deep water exceeding 11 μM (Table 1) (Scranton, 1988); (Reeburgh et al., 1991). 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 a reference site (no seep influence). Given the high methane oxidation rates, and the corresponding high turnover of, on average, approximately 1–2 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}) from Section 3.3.

Table 1. Methane concentrations, oxidation rates, and residence times (Schubert, 2004).

Location depth (m)	Methane concentraion nM			Methaneoxidation rate nM/d			Residence time day		
	1–150 m	150–300 m	300–end	0–150 m	150–300 m	300–end	0–150 m	150–300 m	300–end
250 (seep)	34	736		0.08	2.05		425	359	
600 (seep)	262	3585	8443	0.34	6.99	16.15	771	513	523
2000 (off seep)	269	3326	11318	1.04	10.3	33.4	259	323	339

4 CONCLUSIONS

It is estimated that the Black Sea contains a total of 96 Tg of methane (Reeburgh et al., 1991). From Table 1, the methane oxidation rate is calculated as 60 Tg yr^{-1}, based on a methane residence time of approximately 1–2 years, a relatively short period of time. Assuming steady state, this oxidation rate is in balance with a methane-carbon production of 100 g C m^{-2} yr^{-1}, which is in good agreement to the primary production of 240 C m^{-2} yr^{-1} reported by Sorokin (2002). Typically, approximate 10–20% of primary productivity results in a net system carbon production (i.e. 24–48 g C m^{-2} yr^{-1}); suggesting other sources of methane besides from methanogenesis.

Preliminary conclusions indicate that methane plumes from deep water sources, while perhaps strong (e.g. the $\sim$0.025 Tg yr^{-1} estimated from the single, deep plume in this study), stop well below the surface where the methane is oxidized to CO_2 before reaching the atmosphere. Depending on the initial bubble size, methane reaches the surface only in shallow sites (<about 200 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, and may allow slightly deeper sources to reach the atmosphere. However, the high oxidations rates and low diffusivities lead to surface flux estimates of less than 70 Mg yr^{-1}, allowing us to conclude that the Black Sea is not, compared to a worldwide release of 500 Tg yr^{-1}, a significant contributor of methane to the atmosphere.

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