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Methane emission from high-intensity marine gas seeps in the Black Sea into the atmosphere

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[1] Submarine high-intensity methane seeps have been surveyed in the Sorokin Trough and Paleo Dnepr Area in the Black Sea from May to June, 2003 to estimate the sea-air methane flux. The Sorokin Trough mud volcano area in around 2080 m water depth shows no direct effects on the methane concentration in the surface water and the atmosphere (average methane saturation ratios (SR) of 143%). The average sea-air methane flux can be determined as 0.2–0.57 nmol m^{-2} s^{-1}, using two different sea-air gas exchange models; mean wind speed were extraordinary low throughout the cruise (1.16 m s^{-1}). The investigations in the Paleo Dnepr Area (60 to 800 m water depth) reflects a more diverse pattern. Spots of high methane concentrations in the surface water have been recorded above a seep location in around 90 m water depth (SR up to 294%). The air-sea methane flux above this seep site (0.96–2.32 nmol m^{-2} s^{-1}) is 3 times higher than calculated for the surrounding shelf (0.32–0.77 nmol m^{-2} s^{-1}) and 5 times higher than assessed for open Black Sea waters (water depth > 200 m, 0.19–0.47 nmol m^{-2} s^{-1}). **Citation:** Schmale, O., J. Greinert, and G. Rehder (2005), Methane emission from high-intensity marine gas seeps in the Black Sea into the atmosphere, *Geophys. Res. Lett.*, *32*, L07609, doi:10.1029/2004GL021138.

1. Introduction

[2] The Black Sea is the world largest anoxic basin with a unique water column stratification caused by the influx of saline water from the Mediterranean Sea and freshwater from rivers (mainly Danube, Dnepr and Dnyestr). This induces a strong stratification of the water column with a permanent pycnocline at around 150 m water depth. The limited exchange between these separated water masses leads to anaerobic conditions in the lower zone which is highly enriched in geochemically reduced species, such as CH_4, H_2S and NH_4. The anoxic water column of the Black Sea represents the world largest semi-closed water reservoir of dissolved methane. Methane itself is of particular interest because of its rising atmospheric concentrations and its contribution to global warming [*Lelieveld et al.*, 1998].

[3] Numerous scientific studies lead to a complex figure of the Black Sea methane cycle [e.g., *Ivanov et al.*, 1989; *Reeburgh et al.*, 1991]. Reeburgh et al. compiled a simple methane budget for the Black Sea. They suggest that microbial methane generated in the shelf and slope sediments is the major methane source, which is balanced by anaerobic oxidation of methane in the anoxic water column (4.7 Tg yr^{-1}). Less important for the methane budget are the microbial oxidation of methane in the oxic water column ($0.3 \cdot 10^{-3}$ Tg yr^{-1}) and the anaerobic oxidation in abyssal sediments ($0.4 \cdot 10^{-3}$ Tg yr^{-1}), the outflow through the Bosporus ($0.03 \cdot 10^{-3}$ Tg yr^{-1}) and the export into the atmosphere (0.07 Tg yr^{-1}). Thus, according to Reeburgh et al. only 1.5% of methane produced in the Black Sea is emitted into the atmosphere. The water column oxidation rate given by *Reeburgh et al.* [1991] suggests a short turnover time of methane of about 20 years. The general water column methane concentration below 500 m water depth is fairly homogeneous (around 11 μM (*Reeburgh et al.* [1991] and unpublished data of the CRIMEA project)).

[4] Except the work by *Reeburgh et al.* [1991], little information about the role of the Black Sea as a source of the atmospheric methane has been presented. *Dimitrov* [2002] suggests that about 0.36 to 1.6 Tg yr^{-1} CH_4 is transported into the atmosphere from the Black Sea continental shelf. His calculations are based on hydro-acoustic quantifications of gas seepages, determination of seabed flux rates, and the survival time of uprising methane bubbles in the water column. In contrast, *Amouroux et al.* [2002] infer a shelf emission between 0.019 and 0.032 Tg yr^{-1} and a total emission from the Black Sea surface water of 0.106 to 0.189 Tg yr^{-1}, based on surface water methane measurements similar to the approach used in our study. These different estimates clearly show that additional studies are needed to understand the Black Sea methane cycle and its atmospheric source strength.

[5] Here, we will discuss the contribution of different seep locations (Paleo Dnepr Area and Sorokin Trough) and evaluate their role as a methane source to the atmosphere. We will present methane concentrations of the surface water and atmosphere and calculate the flux of methane based on the sea-air gas exchange models of *Liss and Merlivat* [1986] (LM-86) and *Wanninkhof* [1992] (W-92).

2. Study Areas

[6] Our research cruise CRIMEA 2003 with RV *Professor Vodyanitsky* took place from May 15th to July 1st, 2003 and was focused on the investigation of sub-marine high-intensity methane seeps which continuously release high amounts of free gas (mainly methane) from the seabed into the water column (http://www.crimea-info.org/). These gas bubble releasing seep sites are widely distributed on the shelf and at the shelf edge of the Black Sea, but a few have been reported in deep water as well [*Egorov et al.*, 1998; *Dimitrov*, 2002].

[7] Main study areas of the CRIMEA project are the paleo delta area of the Dnepr river and the Sorokin Trough

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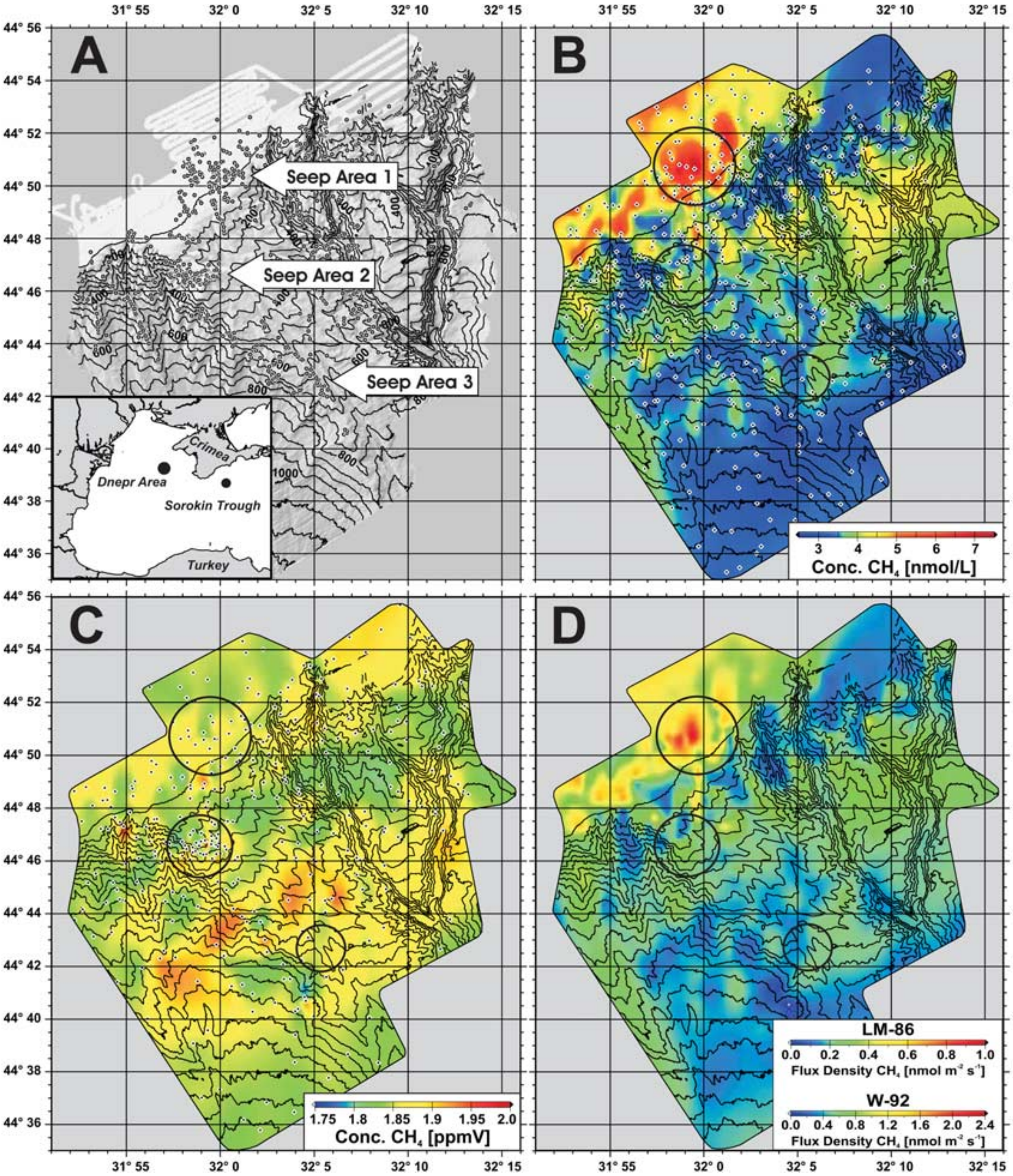

Figure 1. (a) The two CRIMEA study areas: the shallow-water Dnepr paleo delta and the deep-water Sorokin Trough mud volcano region. Bathymetric map of the Dnepr paleo delta and the three main seep areas; black dots represent active bubble seeps recorded during the cruise. (b) Dissolved methane concentration in the surface water and (c) the overlying atmosphere and (d) the results of the methane flux density according to the sea-air gas exchange models of *Liss and Merlivat* [1986] and *Wanninkhof* [1992] in the Paleo Dnepr Area. Black diamonds in Figures 1b and 1c represent locations of individual water and air measurements, respectively. The black open circles emphasize the Seep Areas 1, 2 and 3.

south of the Crimea peninsula (Figure 1a). Detailed hydro-acoustic studies in the Paleo Dnepr Area show that active seeps are distributed along the entire shelf and shelf edge, down to a water depth of 725 m, which represents almost exactly the phase boundary for pure methane hydrate at the ambient temperature and salinity conditions [*Dickens and Quinby-Hunt*, 1994]. Three high-intensive sites have been investigated in detail: Seep Area 1 in about 90 m water depth, Seep Area 2 in 220 m water depth, and Seep Area 3 in about 600 m water depth. In the Sorokin Trough some mud volcanoes also show hydroacoustic anomalies (flares), which provides evidence for the release of free gas even in 2080 m water depth (Dvurechenskii mud volcano). Flare imaging indicates that the gas rises more than 1000 m (unpublished data of the CRIMEA project). These notable bubble emissions have only been found periodically, and thus seem to occur just intermittently.

3. Results and Discussion

[8] The spatial distribution of the concentrations of methane in the surface layer and the methane mole fraction

Table 1. Methane Flux Density From Different Surface Water Types of the Black Sea and Values of Already Published Data

Water Type	Area	Flux Density [nmol m^{-2} s^{-1}] LM-86	W-92	Reference
open waters	Sorokin Trough	0.20	0.57	This study
water depth > 200 m	Dnepr Area	0.19	0.47	This study
	NW Black Sea	0.34	0.58	*Amouroux et al.* [2002]
	Central Black Sea	0.31		*Reeburgh et al.* [1991]
shelf waters	Dnepr Area	0.32	0.77	This study
water depth < 200 m	NW Black Sea	0.37	0.61	*Amouroux et al.* [2002]

in the overlying atmosphere of the Paleo Dnepr Area are given in Figures 1b and 1c. The results of the methane flux calculations are illustrated in Figure 1d. The CH_4 fluxes after LM-86 and W-92 were calculated on the base of the average wind speed of 1.16 m s^{-1}. The average sea surface temperatures were 19.51°C and 19.36°C and the average salinities were 17.88‰ and 17.79‰ for the Paleo Dnepr Area and the Sorokin Trough, respectively.[1]

[9] Table 1 shows the mean flux density from different surface water types and areas of the Black Sea investigated during the CRIMEA cruise in 2003. For comparison values of already published data from the Black Sea are shown [*Amouroux et al.*, 2002; *Reeburgh et al.*, 1991].

[10] The surface water methane distribution displayed in Figure 1b shows a strong dependency between the individual water depth of different seep sites and their influence on the surface water methane concentration. Shelf seeps (Seep Area 1) in around 90 m water depth directly affect the methane distribution of the surface water as indicated by the coincidence of seep positions and highest methane concentrations. This direct correlation is also supported by water column investigations above Seep Area 1 during the same cruise. A plume indicated by high concentrations of methane can be traced from the sea floor to near surface waters (data not shown). Increased surface water methane concentrations away from any seep influence could result from microbial methane generation in shelf sediments [*Ivanov et al.*, 2002]. Seeps in water depths greater than approx. 150 m (Seep Area 2, 3 and mud volcanoes in the Sorokin Trough) do not show any significant imprint on the surface water methane content. Surface concentrations above these deeper seep sites are fairly homogeneous and similar to areas where no high-intensity seeps exists. The most obvious reason for this is the dissimilarity and thickness of the water layer above the seeps.

[11] Gas will be continuously dissolved during the ascent of the bubble at the gas/water interface. The rise velocity of approximately 15m/min [*Leifer et al.*, 2000] implies that the lifetime of bubbles is short enough to exclude oxidative consumption as a process influencing bubble behavior and bubble-mediated gas transport. However, anaerobic methane oxidation is responsible for intense methane consumption throughout the entire anoxic zone [*Reeburgh et al.*, 1991]. The short turnover time for methane in the order of 20 years [*Reeburgh et al.*, 1991] and the uniform water age of 1000 yr between 300 and 1700 m water depth [*Östlund*, 1974] implies that the dissolved methane fraction below the pycnocline will be oxidized rather than transported to the sea surface. Another boundary for methane migrating upward is the oxic/anoxic interface, where consumption rates can be extraordinary high, and the microbial oxidation of methane in the oxic water [*Ivanov et al.*, 2002; *Reeburgh et al.*, 1991]. Thus, only shallow seeps which release methane close to the sea surface can bypass methane oxidation and have a direct influence on the local methane emission to the atmosphere.

[12] Compared to the surface water methane concentrations, atmospheric methane was more or less uniform during the cruise period reaching an average value of 1.86 ± 0.03 ppmv (Figure 1c). These values are slightly higher than the results reported for the same timeframe by U.S. NOAA global sampling networks (1.78 to 1.83 ppmv) from the monitoring site at the Azores, which we choose because it is almost the same latitude and far from anthropogenic methane sources (http://www.cmdl.noaa.gov/ccgg/iadv/). In any case, methane escaping from the sea surface into the air will be diluted rapidly in the atmosphere and influences are difficult to trace by atmospheric methane measurements. The source strength of Seep Area 1 is not high enough to be responsible for increased atmospheric concentrations as observed in the southern part of the Paleo Dnepr Area. A reasonable explanation for this phenomenon is an impact of anthropogenic sources located on land. Nevertheless, our data show that the Black Sea shelf in particular but the open water also are a significant source of atmospheric methane due to its constant oversaturation with respect to the atmosphere.

[13] The SR ranges from 98 to 294% in the Paleo Dnepr Area and shows an average value of 143% in the Sorokin Trough. The methane distribution and SR in surface waters above the Sorokin Trough is very homogeneous (data are not shown). At Seep Area 1 in the Dnepr Area, the surface water reaches SR of 294% whereas the surrounding homogeneous water shows an average ratio of 148%. Our data suggest that the SR of the open water is comparable between the two study areas and possibly reflect a rather homogeneous pattern over the entire Black Sea. However, our SRs of the Paleo Dnepr Area are relatively low compared with data published by *Amouroux et al.* [2002] who observed SRs for the NW Black Sea ranging from 173% to 10.500%. The authors describe average values of 5.340% for the Danube river plume, 567% for the shelf area and 401% for the open water. Samples taken by *Amouroux et al.* [2002] in the vicinity of the Paleo Dnepr Area show an average SRs of around 300% which indicates that they sampled above seep influenced areas comparable with Seep Area 1. Unfortunately they do not give any indications where samples exactly where taken or if they sampled above active seep areas.

[1]Auxiliary material is available at ftp://ftp.agu.org/apend/gl/2004GL021138.

[14] The sea-air methane flux calculations (Figure 1d) show that methane emission from Seep Area 1 (0.96–2.32 nmol m^{-2} s^{-1}) is 3 times higher than from the surrounding shelf (0.32–0.77 nmol m^{-2} s^{-1}) and 5 times higher than from the open water (0.19–0.47 nmol m^{-2} s^{-1}). The average sea-air methane flux determined for the Sorokin Trough was 0.2–057 nmol m^{-2} s^{-1}. It has to be emphasized that the average wind velocity were exceptionally low during the entire cruise.

[15] We have to consider that our dataset quantifies only the flux caused by methane dissolved in surface waters. Free gas which reaches the surface layer can not be detected by the equilibrator system. This is of crucial interest for Seep Area 1 where bubbles have been visually observed at the sea surface. Thus, the gas flux into the atmosphere at this seep site could be underestimated. On locations where remaining gas bubbles reach the surface, our approach can only yield a lower limit of the direct methane flux caused by the seep.

4. Conclusions

[16] Recent publications describe a direct contribution of submarine gas seeps to the global atmospheric methane budget [*Milkov et al.*, 2003; *Kopf*, 2003]. This hypothesis could not be supported by our results, at least not for the entire Black Sea region. Our findings suggest that only shallow seeps, in water depth shallower than 100 m, affect the surface water methane concentration and the direct local emission into the atmosphere. High intensity seep sites below this boundary show no regional influence on the surface concentration.

[17] Another interesting finding is that the methane oversaturation in the open Black Sea surface waters does not differ considerably from that found in other highly productive areas [*Cynar and Yayanos*, 1993; *Bange et al.*, 1994; *Rehder et al.*, 2002], despite of the large methane reservoir in the underlying anoxic water masses. The different redox regimes in connection with the hydrographic structure in the Black Sea provide an effective mechanism to hamper evasion from this reservoir into the atmosphere. Thus, gas bubble transport, providing a rapid pathway through the water column and mostly unaffected by oxidative consumption, might be a major contribution to the methane flux to the atmosphere from the sea floor.

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