NATURAL GAS IN MARINE ENVIRONMENT OF THE BLACK SEA AND ITS EFFECT ON CLIMATE CHANGE

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For almost 30 years serious interest has been directed toward natural gas as a potential energy and factor in global climate change. The principales sources of natural gas in marine environment are the transformations of organic matter in the earth's crust, microbial decomposition of organic substances and reduction of mineral salts. Besides the previously mentioned sources, gas hydrates are another extremely promising source of gas hydrocarbons on the sea battom. The components commonly found in natural gas released from marine environment of the Black Sea are methane and its homologues, carbon dioxide, hydrogen sulfide, nitrogen, and also helium. From these gases, carbon dioxide and methane are highly potent greenhouse gases. Their emission appeared to be linked to climate changes and species extinction both in the ocean and on continental margins. To the extent possible, this paper constitues a review on investigated deposits of natural gas from Black Sea and its effect on climate change from this area. An instantaneous release of natural gas could have an impact on atmospheric composition and thus on the radioactive properies of the atmosphere that affect global climate.

1. INTRODUCTION

Climate change comprises the long-term (on the decadal time-scale) changes in the coupled ocean−atmosphere system parameters due to natural and human causes. The best known example of climate change is the global warming. Recent studies have shown that climate change (global warming) will lead to a sea-level rise of several millimetres per year as well as a rise in the frequency and intensity of storms. The combined effect of these two effects could have serious consequences (such as severe coastal flooding and shoreline erosion). In general, climate change is expected to lead to: higher temperatures; melting of glaciers and land ice; thermal expansion of ocean water; sea-level rise; changes in the intensity, frequency and direction of storms; changes in rainfall and evaporation; sea-temperature rise and changed currents (which may affect the fishing areas); changes in coastal and open-sea ecosystems, for the foregoing reasons.

The probable effects of climate change listed above are of great importance for many uman activities and need to be constantly observed and predicted.Public concern about global warming mostly focuses on carbon dioxide , the most prevalent greenhouse gas. Methane (CH_4), the major component of natural gas, is second in importance as a greenhouse gas. Methane concentration in the atmosphere has more than doubled during the last 30 years.Its current atmospheric concentration of 1.7 ppm by volume, up from 0.7 ppm in preindustrial times, is much lower than the 345 ppm of carbon dioxide , up from 275 ppm. But one molecule of methane traps approximately 30 times as much heat as does carbon dioxide.The heating effect at the atmospheric methane increase is approximately 1/3 that of the carbon dioxide increase.[1,2]. Continued increase in atmospheric methane concentrations at the current rate of approximately 1% per year is likely to contribute more to future climatic

change than any other gas, except carbon dioxide [3] and may significantly contribute to a negative feedback system with unpredictable consequences for the whole chemistry of the atmosphere [4].

Aside from being an important greenhouse gas, methane also affects the chemistry and oxidation capacity of the atmosphere, for example, by influencing concentrations of tropospheric ozone, hydroxyl radicals and carbon monoxide. In the stratosphere, it is a sink for clhorine, but a source for hydrogen and watervapor. The current burden of methane in the atmosphere is approximately 4700 Tg(1Tg= million tones)[5], and the global annual emission is estimated to be 500Tg with an apparent net flux of 40 Tg/year[3].Wetland and sediment deposits on sea floor have recently been identified as a major source of atmospheric methane .

Previous investigations on the Black Sea have focused primarily on the biogeochemistry of natural gas (in principal on CH_4) in the deep, permanent anoxic basin [5-8]. Methane (CH_4) cycling in the main Black Sea basin has been investigated by Reeburgh *et al*. [8], and is predominantly driven by gas seeps and microbial oxidation in the water column. It was estimated that the CH4 flux to the atmosphere from the Black Sea is about 4.1 Gmol / year. CH4 is an atmospheric trace gas that contributes to 15% of the greenhouse effect and is undergoing atmospheric concentration increases that have slowed down from 1 to about 0·5%per year during the last two decades [9,10,11]. Coastal environments were found to account for 75% of the oceanic emissions to the atmosphere [12], which contributes to about 2% of the global atmospheric emission . The Black Sea is also the largest surface water reservoir of methane (6000 Gmol), which is contained in the anoxic zone of the main basin[3]. In the case of the western Black Sea shelf (Romanian coast), intense eutrophication may lead to the deposition of high amounts of organic matter to the sediment floor, which could provide labile organic carbon and generate favourable reducing conditions for the microbial production of methane [3,12,13,14,15,16]. The geochemistry of methane is therefore of primary importance in the Black Sea ecosystem, where both atmospheric evasion and methane oxidation represent the major sinks [8].

This paper intends to extend the global inventories of CH_4 fluxes to the atmosphere from marine environments and to indicate potential interactions between these fluxes and the biogeochemical changes on the western shelf of the Black Sea. We investigated the distribution of CH_4, in surface waters of the western Black Sea, mainly influenced by the Danube River inflow. CH_4 mixing rate in the atmosphere above the sea were also measured in order to accurately determine the saturation of this gas in surface shelf waters. Finally we have estimated flux densities from the western shelf and extrapolated the emission rates of the entire Black Sea basin during the summer period for the methane gas.

2. MATERIALS AND METHODS

The investigation of the near-shore waters was focused on Constanza Bay (Romanian coast, west of the shelf), along a 150 km coastal water reach between Eforie Sud , Constanza and Sulina. Seawater temperature and salinity were monitored continuously using a conductimeter Phylips type PW 9501 101,the conductimeter was calibrated in order to obtain direct salinity values according to the International System of Units. For the measurements of the gas methane a special sampling system was used. The concentration in atmosphere and dissolved CH_4 in the surface water was obtaining using a system involving gas chromatography (5890 A , Hewlett Packard) equiped with a packed stainless steal Porapak-Q column and molecular sieve 5A packed column, with a flame ionization and conductivity

detectors.Calibrations were performed using standard gas mixtures for CH_4. Methane saturation ratio (SR) between surface waters and overlying atmosphere was directly calculated from the mixing ratio of gas measured in equilibrated air (X_e) and the ambient air (X_a) .

3. RESULTATS AND DISCUSSIONS

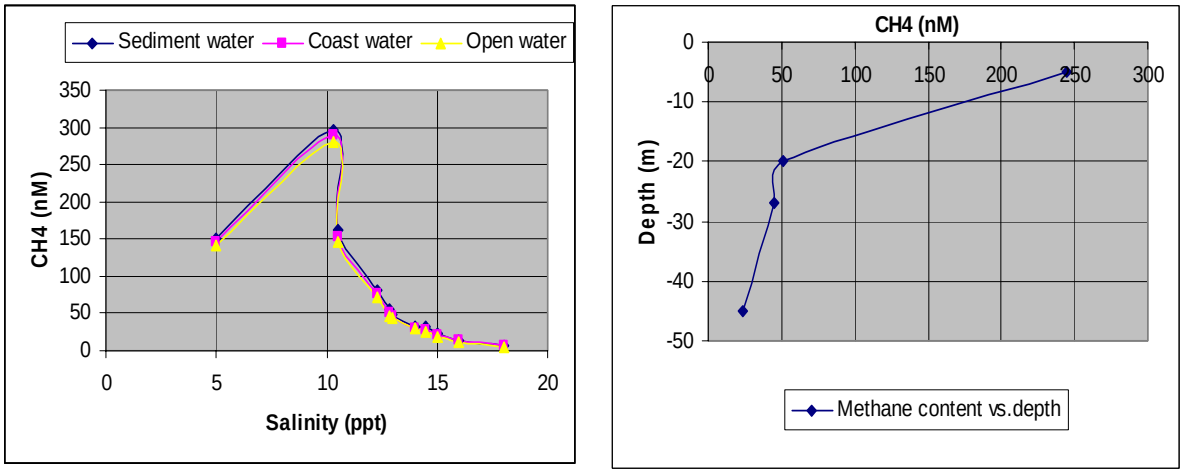
The CH_4 concentrations determined have shown that the atmospheric CH_4 mixing ratio was fairly constant throughout the cruise, averaging 1·85±0·06 ppmv (Table 1).

Table 1.Methane distribution in different surface water types of the western Black Sea and comparison literature data

	Average Concentrations (nM)	Average mixing ratio (MR, ppmv)	Average saturation ratio (SR,%)	Literature SR (%)
CH_4 in				(%)
Open water (N═ 20)	9.4.1±4.7	1.80	400	120[a]
Water from coastal area(N═ 20)	14.1±9.6	1.87	562	395[b]
Water from sediments (N═ 20)	132±40	1.94	534	-
Reeburgh et aL (1991)	10	-	200-500	-

[a]Bange et al (1994)[ ]; [b]Bange et al (1996a)[ ]

The average mixing ratio is slightly higher than the results raported in literature data [8,16,17] These values ranging from 1·73 to 1·80 ppmv The mixing ratio obtained for the main deep basin average 1·80 ppmv is in good agreement with literature These high values indicate that both the water from marine sediment and water from coastal area are important sources of atmospheric CH_4. CH_4 concentrations measured in the western Black Sea surface waters were mainly dependent on salinity(figure 1. a) and on the water mass sampled, ranging from 4.2 nM above the main, deep anoxic basin to 250 nM in water from sediments(fig.1 b).



a) b)

Figure 1.Methane concentrations in surface waters of the west Black Sea coastal area as a function of water salinity a) and depth b).

CH_4 concentrations in open Black Sea waters average 9.4 nM and are very similar to those obtained several years ago by Reeburgh *et al.* (1991)[8] at *c.* 10 nM (Table 1). CH_4 concentrations along the estuarine salinity gradient show a nonconservative behaviour.

Concentrations decrease rapidly from salinity 8 to 18 without following a linear mixing curve (Figure 1 a). The apparent CH_4 loss during the estuarine transfer is probably due to both ventilation and microbial methane oxidation.Such inverse relationships have also been found in various other estuarine and coastal environments [13,16]. Our data indicate that the west coastal area is an important source of CH4 due probably and to the Danube Delta. To better understand CH_4 sources on the western Black Sea shelf, there were performed the profile of temperature vs. depth(figure 2) and the salinity profile vs. depth(figure 3).Also it was determined the oxygen content in waters vs. depth(figure 4). At the Constantza front area within the first 5m a slight increase of the salinity with deph shows the accurrence of the surface layer corresponding to along western coastal.CH_4 concentrations decreased sharply abruptly from 245 nM in the surface layer to 24-45 nM in the water column (figure 1.b).

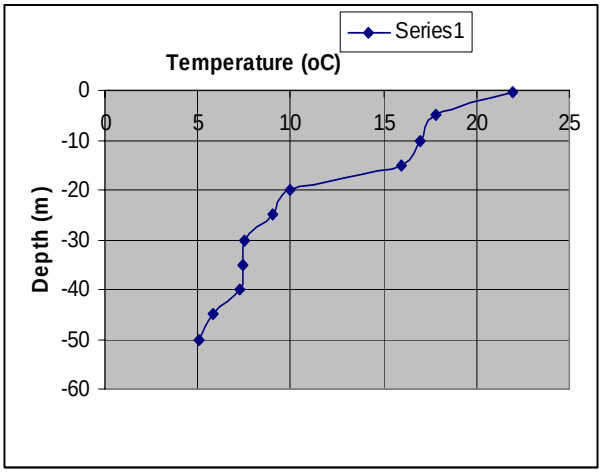


Figure 2. Temperature profile vs. depth in coastal waters on the western Black Sea shelf

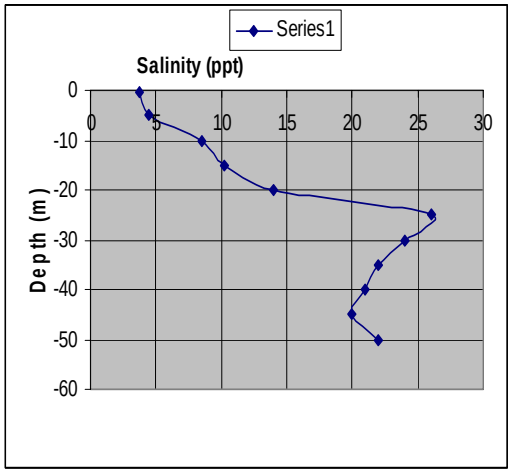


Figure 3. Salinity profile vs. depth in coastal waters on the western Black Sea shelf.

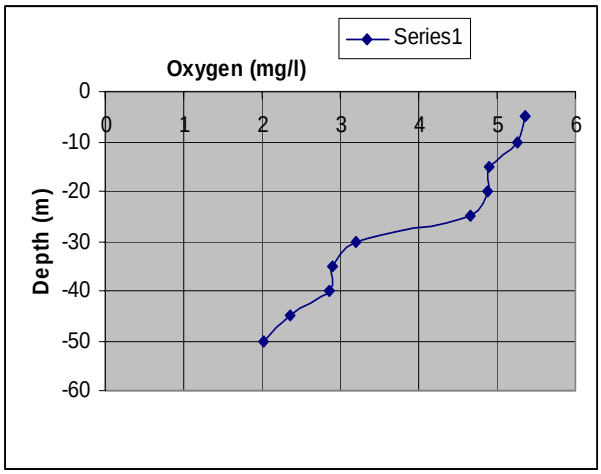


Figure 4. Oxygen content vs. depth on the western Black Sea shelf

Oxygen concentration decreased from 5.45 mg/l in the surface layer to 2 mg/l in the water column (figure 4).

These data cleary demonstrate that a large amount of methane there is at surface water which can then be easly ventilated to the atmophere.Although concentrations were about 10 times lower than at surface, CH_4 was supersaturated in the entire water column. Production of CH_4 within the near-shore water column has been observed previously and may result from the presence of reducing microenvironments [14,15]

Shelf sediments were also found to be a significant source of CH4 to surface waters during the summer of 2003 and could explain the high supersaturation in the entire shelf investigated (average 534%). High SRs were observed in open surface waters of the NW Black Sea, with an average of 400%. These values are in agreement with those obtained by Reeburgh *et al*. (1991)[8] in surface waters of the central part of the Black Sea deep basin, which were found to range from 200 to 500%.

The studies performed have both outlined the role of the shelf slope sediments on the Black Sea CH_4 budget and have estimated that the sediments release an amount range from 665 μmol m^{-2} day^{-1} and 540 μmol m^{-2} day^{-1} of CH_4. Our measurement shown that the CH_4 emission rate from the Black Sea, extrapolated from the flux density values obtained during the summer period, is 5.5-6.8 to 11·7 Gmol $yr^{--1.}$ These emission rates are about 1·5 to 3 times higher than those estimated by Reeburgh *et al*. (1991)[8].

This difference cannot only be explained by seasonal trends or differences in air–sea exchange, but also represents the important contribution of CH_4-enriched surface waters in western shelf of the Black Sea.The researches [17-19] have indicated that the anaerobic oxidation of methane(AOM) and of other gas hydrocarbons take place in anoxic marine sediments and waters of the Black Sea. Our measurements shown that there are three different sources which release methane in surface waters and subsequently to the atmosphere: CH_4 seeps in the slope of the main , deep anoxic basin, methanogenesis in bottom shelf sediments and CH_4 inflo from the Danube delta and estuary. The changes in the western coastal environment of the Black Sea is also due to the anthropogenic disturbances such as nutrient load and chemical pollution , on the production of biogenic gases of atmospheric and climate interest[17-21].

4. CONCLUSIONS

In the present study, we have determined the concentrations and atmospheric fluxes of CH_4 in the western Black Sea shelf. This study also addresses the potential importance of biogeochemical changes in the coastal environment of the Black Sea, due to anthropogenic disturbances such as nutrient load and chemical pollution, on the production of biogenic gases of atmospheric and climate interest.Three different sources release CH_4 in surface and column waters and subsequently to the atmosphere: CH_4 seeps in the slope of the main, deep anoxic basin, methanogenesis in bottom shelf sediments, and CH_4 inflow from the Danube delta and estuary. In order to assess the long-term effect of the biogeochemical changes in the western Black Sea on the production of biogenic gases, further work, focussing on the seasonal and interannual variability, is now necessary.

REFERENCES

[1]R.E. Dickinson and R.J. Cicerone, Nature, 319 (1986), 109-115;
[2]R.J.Cicerone, H.B. Singh and J.T. Kiehl, J. Geophys.Res. 90 (1985), 5547-5566;

[3] R.J.Cicerone, and R.S.Oremland, Biochem. Cycles,2, (1988), 299-327;
[4] H.Neue, BioScience, 43 (7), (1993), 466-473;
[5] M.N.W ahlen, R. Henry, B.Deck et all, Science, 245, (1989), 286-290;
[6] Hunt, J. M. 1974 Hydrocarbon Geochemistry of Black Sea. In *TheBlack Sea—Geology, Chemistry and Biology* (Degens, E. T. & Ross,D. A., eds). American Association of Petroleum Geologists,Memoir 20, pp. 499–504.
[7] Scranton, M. I. 1977 The Marine Geochemistry of Methane. Ph.D. Thesis, W.H.O.I./M.I.T. Joint Programme, Woods Hole, 251 pp.
[8] Reeburgh, W. S., Ward, B. B., Whalen, S. C., Sandbeck, K. A., Kilpatrick, K. A. & Kerkhof, L. J. 1991 Black Sea Methane Geochemistry. *Deep-Sea Research Part A* 38, S1189–S1210.
[9] Steele, L. P., Dlugokencky, E. J., Lang, P. M., Tans, P. P., Martin, R. C. & Masarie, K. A. 1992 Slowing down of the Global Accumulation of Methane during the 1980s. *Nature* 358,313-316;
[10] Matthews, E. 1994 Assessment of Methane Sources and their Uncertainties. *Pure and pplied Chemistry* 66, 154–162.
[11] Houghton, J. T., Meira Filho, L. G., Callander, B. A., Harris, N., Kattenberg, A. & Maskell, K. (eds) 1996 *Climate Change, 1995:The Science of Climate Change*. Cambridge University Press,Cambridge, 572 pp.
[12] Ivanov, M. V. & Lein, A. Yu. 1991- Causes of Appearance of Anaerobic Conditions in Pre-bottom Waters of the North-Western Shelf of the Black Sea. *UNESCO Technical Papers in MarineScience*, 64, Proceedings of the COMAR Interregional Science Conference, UNESCO, Paris, 21–25 May 1991, pp. 232–245.
[13] Scranton, M. I. & McShane, K. 1991 Methane Fluxes in the Southern North Sea: the role of European rivers. *Continental Shelf Research* 11, 37–52.
[14] Bange, H. W., Rapsomanikis, S. & Andreae, M. O. 1996*a* Nitrous Oxide in Coastal Waters. *Global Biogeochemical Cycles* 10, 197–207.
[15] Wiesenburg, D. A. & Guinasso, Jr. N. L. 1979 Equilibrium Solubilities of Methane, Carbon Monoxide and Hydrogen in Water and Seawater. *Journal of Chemical Engineering Data* 24,356–360.
[16] Bange, H. W., Bartell, U. H., Rapsomanikis, S. & Andreae, M. O. 1994 Methane in the Baltic and North Seas and a Reassessment of the Marine Emissions of Methane. *Global Biogeochemical Cycles* 8, 465–480.
[17] Bange, H. W., Dahlke, S., Ramesh, R., Meyer-Reil, L. A., Rapsomanikis, S. & Andreae, M. O. 998 Seasonal Study of Methane and Nitrous Oxide in the Coastal Waters of the Southern Baltic Sea. *Estuarine, Coastal and Shelf Science* 47**,** 807–817.
[18] Ivanov, M. V., Polikarpov, G. G., Lein, A. Yu., Gal'chenko, V. F., Yegorov, V. N., Gulin, S. B., Gulin,M. B., Rusanov, I. I., Miller, Yu. M. & Kuptsov, V. I. 1991 Biogeochemistry of the Carbon Cycle in an Area of Methane Seeps in the Black Sea. *Transactions ofthe USSR Academy of Sciences: Earth Science Sections* 321A**,**165–170.
[19] De Angelis, M. A. & Lilley, M. D. 1987 Methane in Surface Waters of Oregon Estuaries and Rivers. *Limnology and Oceanography* **32,** 716–722.
[20] Ivanov, M. V., Pimenov, N. V., Rusanov, I. I. & Lein, A. Yu. 2002 Microbial Processes of the Methane Cycle at the North-Western Shelf of the Black Sea. *Estuarine, Coastal and Shelf Science* 54**,**589–599.
[21] De Laune, R. D., Smith, C. J. & Patrick, Jr. W. H. 1983 Methane Release from Gulf Coast Wetlands. *Tellus* 35B, 8–15.