Atmos. Chem. Phys., 6, 5173–5182, 2006
www.atmos-chem-phys.net/6/5173/2006/
© Author(s) 2006. This work is licensed
under a Creative Commons License.

Atmospheric Chemistry and Physics

Effects of methane outgassing on the Black Sea atmosphere

K. Kourtidis[1], **I. Kioutsioukis**[1], **D. F. McGinnis**[2], **and S. Rapsomanikis**[1]

[1]Laboratory of Atmospheric Pollution and Pollution Control Engineering of Atmospheric Pollutants, Dept. of Environmental Engineering, Democritus University of Thrace, P.O. Box 447, 67100 Xanthi, Greece
[2]Surface Waters – Research and Management, Swiss Federal Institute of Aquatic Science and Technology, Eawag, 6047 Kastanienbaum, Switzerland

Received: 7 February 2006 – Published in Atmos. Chem. Phys. Discuss.: 9 May 2006
Revised: 25 September 2006 – Accepted: 6 November 2006 – Published: 14 November 2006

Abstract. Methane in air and seawater was measured in the Eastern Black Sea during the 10–18 December 1999 BIGBLACK project cruise. The measurements allowed for the calculation of supersaturation ratios and methane fluxes across the air-sea interface. CH_4 mixing ratios in air were generally in the 1.8–2.0 ppmv range, while surface (4 m depth) seawater concentrations varied from 4 to 93 ppmv. Above active seep areas, the water was supersaturated to around 500% with respect to the overlying atmosphere. Accordingly, flux densities varied greatly and were up to 3300 umol m^{-2} day^{-1}. In the Sevastopol harbour, supersaturations up to around 3000%, similar to those at the Danube Delta, were observed, while in the Istanbul harbour supersaturations could not be determined because the very high values of water concentrations led to detector saturation. Simple modelling shows that the observed fluxes do not have any substantial impact on the methane content of the Black Sea atmosphere, as they would only raise its concentrations by less than 50 ppt. On the other hand, calculations performed as part of the CRIMEA project show that mud volcano eruptions could episodically raise the methane concentrations well above their regional background for several tens of kilometres downwind. These calculations, which also apply to mud volcano eruptions elsewhere on the globe, indicate that the spatial extend and the magnitude of the atmospheric perturbation is such that its observation might lie within the capabilities of existing satellite instrumentation such as SCIAMACHY on ENVISAT.

Correspondence to: K. Kourtidis
(kourtidi@env.duth.gr)

1 Introduction

Methane is an important greenhouse gas and a precursor of tropospheric ozone (e.g. IPCC, 2001; Lelieveld et al., 1993, 1998). It is produced in a variety of thermogenic and biological methanogenic processes, some of which occur on geologic time scales, while others on much shorter ones. As a result of these processes, large variations of the atmospheric methane abundance might be expected, especially if large reservoirs become unstable. Such reservoirs include methane hydrates (e.g. Kvenvolden, 1993). Another important pathway for degassing buried sediments appears to be episodic mud volcano eruptions (e.g. Dimitrov, 2002; Kopf, 2002) and continuous seepage over wide areas as well as over localised gas vents (e.g. Etiope and Klusman, 2002). Underwater seepages have been investigated by many authors in various parts of the world (e.g. Judd et al., 1997; Hornafius et al., 1999; Clark et al., 2000; Klusman et al., 2000), and have been found to result in elevated methane concentrations in the surface waters overlying these seeps (e.g. Cynar and Yayanos, 1992; Ward, 1992).

The Black Sea has received attention as a target of investigations on methane because of the large amounts of methane trapped in the anaerobic sediments and the hydrates present underneath these sediments. Under normal conditions, methane is vented from the sediments to the overlying water through seeps; some of this methane reaches the water-air interfaced unoxidised and subsequently escapes to the atmosphere, although most of it is consumed from bacterial activity within the water column (e.g. Durisch-Kaiser et al., 2005).

Some investigations of the methane flux from the Black Sea to the atmosphere have already been carried out (Amouroux et al., 2002; Schmale et al., 2005), yielding flux densities generally between 0.19–0.77 nmol m^{-2} s^{-1} (16–66 umol m^{-2} day^{-1}), while above active seeps these might increase to 0.96–2.32 nmol m^{-2} s^{-1}

Published by Copernicus GmbH on behalf of the European Geosciences Union.

(83–200 umol m^{-2} day^{-1}) and above river plumes they might increase even further, up to 5.44 nmol m^{-2} s^{-1} (470 umol m^{-2} day^{-1}).

To derive these fluxes, Amouroux et al. (2002) and Schmale et al. (2005) used the Liss and Merlivat (1986) and the Wanninkhof (1992) parameterisations of the dependency of the transfer velocity k on wind speed u, hereafter referred to as LM86 and W92, respectively. Both parameterisations are quadratic or near-quadratic; W92, for example, parameterises k as a function of u as $k=0.31u_{10}^2(S_c/660)^{-0.5}$, where S_c is the Schmidt number of CO_2 in seawater, 660 is the S_c for CO_2 in seawater at 20°C and u_{10} is the wind speed corrected to 10 m height under neutral conditions.

Recent work, based to a large extent on measurements performed during the GasEx-1998 field experiments (McGillis et al., 2004), has resulted in other, cubic parameterisations, which yield better fits to the data (e.g. Hare et al., 2004 and references therein). Wanninkhof and McGillis (1999), using recent laboratory and field studies, proposed a cubic relationship between air-sea gas exchange and wind speed, $k_{660}=0.028u_{10}^3$, or $k=0.0283u_{10}^3(S_c/660)^{-0.5}$), which, compared with previous calculations using the W92 parameterisation, resulted in a significant increase of the calculated oceanic global annual CO_2 uptake. Fairall et al. (2000) reviewed the theoretical basis of various parameterisation schemes for bulk-to-bulk gas transfer. Since then, McGillis et al. (2001) used eddy accumulation for CO_2 to determine k and showed that k can be described in their study as $k_{660}=3.3+0.026u_{10}^3$, where k_{660} is the k normalised to S_c of 660 cm h^{-1} (which equals the S_c for CO_2 in seawater at 20°C). Other recent work used measurements of dual tracers during the Southern Ocean Iron Fertilisation Experiment SOFex (Wanninkhof et al., 2004) addressing the discrepancies between observational and model-based estimates of CO_2 uptake in the Southern Ocean (see also Feely et al., 2004). Work on the same experiment also considered the effect of wind speed products (Olsen et al., 2005) and addressed the effects of sea-state dependent wave breaking (Woolf, 2005).

In the present study, we applied the LM86, the W92 and additionally, the more recent parameterisation of McGillis et al. (2001), (hereafter referred to as MG01) to cruise data, so as to determine the flux of methane from the Black Sea to the atmosphere.

2 Experiment and methods

The BIGBLACK cruise took place in the waters of the Western Black Sea, in the longitude range 29–32° E and the latitude range 42–45.5° N, onboard the Russian R/V "Professor Vodianitskiy".

Methane in air and seawater was measured with an automated Shimadzu GC/FID equipped with a Weiss equilibrator (Weiss, 1981). Details on the experimental setup can be found in Bange (1994) and Bange et al. (1994), while more details on the function of the equilibrator, as well as a mathematical treatment of the equilibrating processes can be found in Butler et al. (1988, 1989). Briefly, the analysis was performed isothermally on a mol sieve 5Å column at 50°C, with an injector temperature of 60°C and a detector temperature of 280°C. A 10-port valve with two sample loops was used to inject the sample, which was dried before entering the analytical system by means of a 30-cm glass tube filled with Sicapent drying agent. Sampling alternated between ambient air and equilibrated air. Two CH_4 standards from Messer-Griesheim (of 1.57 and 1.96 ppmv methane) were used to calibrate the system during the cruise. Eight duplicate readings from alternate analyses of the two standards gave a response ratio of 1.244±0.012 (1σ), practically identical to the nominal manufacturer's concentration ratio of 1.248. Hence, the first standard, of 1.96 ppmv CH_4, was used extensively throughout the cruise (two to five calibrations daily), while the second one, of 1.57 ppmv CH_4 was used only during the 17 December, 1999. The reproducibility of the measurements, as determined from multiple standard injections during the course of each day, was around 1%.

The inlet for air analyses was around 50 m long, while the inlet from the equilibrated air was around 4 m long. Multiple runs under operating conditions with the 1.96 ppmv methane standard connected to both inlets showed no significant differences that might have risen from inlet wall losses between the two inlets (i.e. the differences were within the 1% reproducibility limits).

The duplicate readings from two different sample loops provided us with the confidence that the precision to see significant local increases in atmospheric concentrations due to high methane fluxes was more than adequate. Methane supersaturations and fluxes were calculated from measurements using the methodology described in detail in Bange (1994) and Bange et al. (1994, 1996), which is based on the approach of Liss and Merlivat, 1986 (LM86), for the transfer velocity calculation. As noted in the Introduction, fluxes were also calculated with the W92 and the MG01 parameterisations.

We note here that LM86, W92 and MG01 normalise their parameterisations with respect to the S_c of CO_2 in seawater at 20°C. Schmidt numbers for methane and CO_2 are rather similar, their difference being –1.7% to 2.6% in the temperature range 0°C to 20°C. Hence LM86, W92 and MG01 parameterisations can be used for methane without modification and without introducing a significant error, since the uncertainty in S_c ranges from 3% to 10%, mainly due to uncertainties in the diffusion coefficient. We note also here that while LM86 note 600 as the S_c of CO_2 at 20°C, W92 and MG01 note 660 as the S_c of CO_2 at 20°C. However, k being a function of either $(S_c/600)^{-0.5}$ or $(S_c/660)^{-0.5}$ (Watson et al., 1991, and references therein), the error from this convention is less than 5%.