The Aegean Sea as a source of atmospheric nitrous oxide and methane

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Abstract

During the EGAMES (*E*vasion of *GA*ses from the *ME*diterranean *Sea*) expedition in July 1993 we determined the concentrations of nitrous oxide and methane in the atmosphere and in the surface waters of the Aegean Sea, the northwestern Levantine Basin, the eastern Ionian Sea and the Amvrakikos Bay. Both gases were found to be supersaturated in all sampled areas. Nitrous oxide was homogeneously distributed with a mean saturation of $105 \pm 2\%$, showing no differences between shelf and open ocean areas, whereas methane saturation values ranged from about 1.2 times (northwestern Levantine Basin) to more than 5 times solubility equilibrium (Amvrakikos Bay estuary). Therefore the Aegean Sea and the adjacent areas were sources of atmospheric nitrous oxide and methane during the study period.

1. Introduction

Nitrous oxide (N_2O) and methane (CH_4) are atmospheric trace gases and contribute about 6% (N_2O) and 15% (CH_4) to the greenhouse effect (Lashof and Ahuja, 1990). Because both nitrous oxide and methane have a long atmospheric residence time (150 years for N_2O, 10 years for CH_4) and because they are key compounds in the chemical reaction cycles of the troposphere and the stratosphere (Crutzen and Schmailzl, 1983; Cicerone and Oremland, 1988) their potential to, directly or indirectly, influence the world's climate is high (Houghton et al., 1990; Lelieveld et al., 1993). The world's ocean contributes significantly to the natural emissions of nitrous oxide (about 20%) (Khalil and Rasmussen, 1992) and modestly in the case of methane (about 2–4%) (Cicerone and Oremland, 1988; Bange et al., 1994). Uncertainties in the estimation of the oceanic fluxes are caused by the strong temporal and spatial variations of the concentrations of dissolved nitrous oxide and methane in the oceanic mixed layer. However, the assessment of the oceanic sources is suffering from the poor data base currently available. In this paper we present our recent measurements of dissolved and atmospheric nitrous oxide and methane in the Aegean, eastern Ionian Sea, and northwestern Levantine Basin. The measurements were conducted as a part of the EGAMES expedition.

2. Study area description and cruise track

The Aegean Sea is a part of the eastern Mediterranean Sea and due to its characteristic hydrographic and bathymetric conditions it is regarded as a separate marginal basin (179,000 km^2, max. water depth 2561 m). Narrow shelf areas (water depths < 200 m) are found in the northern and central Aegean Sea (e.g. the Samothraki and Limnos Plateaus). The cir-
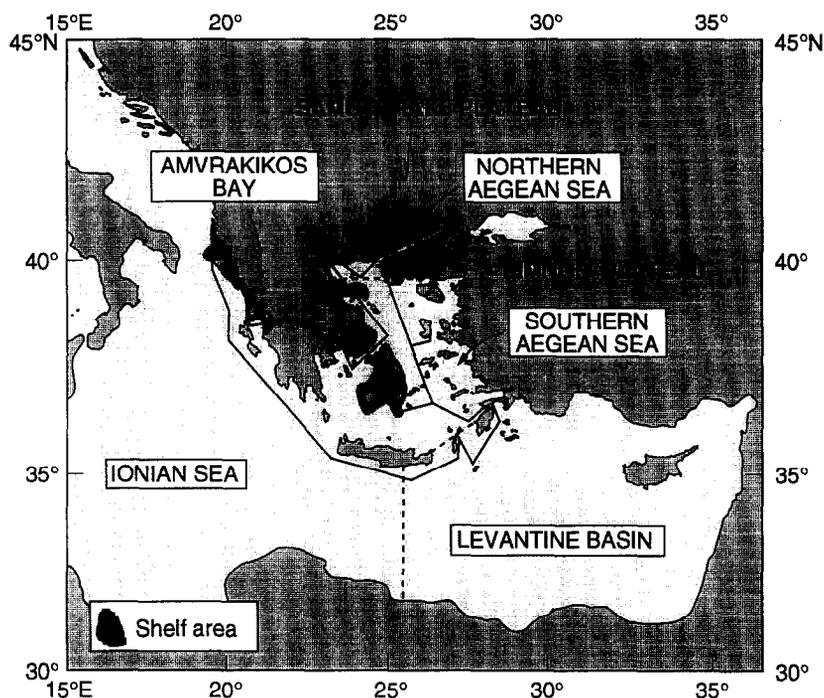
Fig. 1. Cruise track of the R/V Aegaio in July 1993; dashed lines indicate the borders of the different hydrographic regions.

culation of the Aegean Sea is influenced in the northern part by Black Sea waters inflowing through the Straits of Dardanelles and on the southern boundary by exchange processes with waters from the northwestern Levantine Basin and eastern Ionian Sea (The POEM group, 1992; Theocharis and Georgopoulos, 1993; Theocharis et al., 1993). The EGAMES cruise took place in July 1993 on the Greek research vessel R/V Aegaio and followed a cruise track through the Aegean Sea, the northwestern Levantine Basin and the eastern Ionian Sea (Fig. 1). At the end of the cruise, a day was spent conducting measurements in the enclosed area of the estuarine system of Amvrakikos Bay (around 39°N, 21°E).

3. Experimental setup

For the determination of dissolved and atmospheric nitrous oxide and methane we used a gas chromatograph which was equipped with an electron capture detector (ECD) for the detection of N_2O and a flame ionization detector (FID) for CH_4. The setup of our system allowed the frequent determination of

both gases on two columns installed in parallel. Both columns (1.50 m × 3.2 mm for N_2O and 1.80 m × 3.2 mm for CH_4, stainless steel) were packed with washed molecular sieve 5A (mesh 80/100, Alltech Associates, Inc.). The GC-oven was operated with a temperature program that started with the analysis of methane (3 min 60°C), and after heating to 190°C continued with the analysis of nitrous oxide (5 min 190°C). The resulting time resolution (including additional time for heating, cooling and equilibration) for one analysis of nitrous oxide and methane was 25 min. As carrier gases we used a mixture of argon with 5% CH_4 (45 ml min^{-1}, for N_2O) and helium (55 ml min^{-1}, for CH_4). The flame gases for the FID were hydrogen (30 ml min^{-1}) and synthetic air (250 ml min^{-1}). The detectors were held at a temperature of 350°C (ECD) and 250°C (FID).

Ambient air was pumped continuously with a flow of 1.3 l min^{-1} through approximately 40 m polypropylene tubing (OD 9.6 mm, ID 6.4 mm) from the ship's bow into the lab. The location of the air inlet was 6 m above sea level. Seawater was pumped continuously from a depth of 3 m into the lab using the ship's water pump system. By means of a seawa-

ter/air equilibrator developed by R.F. Weiss (Scripps Institution of Oceanography, La Jolla, CA, USA) the seawater was equilibrated with sample air. Our sampling system consisted of four independent sample gas streams (ambient air, equilibrator headspace, two standards) which could be selected for analysis with a system of three magnetic valves. Before analysis, the selected sample gas stream was dried with Sicapent® (phosphorus pentoxide drying agent with indicator, E. Merck, Darmstadt, Germany). After the sample gas stream passed the moisture trap it entered a thermostated (40°C) 10-port gas stream selecting valve (VICI) where a 2-ml sample loop was flushed for 5 min with a sample flow of 25 ml min^{-1} and then injected with the carrier gas. The 10-port gas stream selecting valve was operated in a mode that allowed the injection of the content of two sample loops (2 ml) on two separate columns connected to two separate detectors. The switching of the valves and the GC start were controlled by a computer program (E-Lab, OMS Tech.) thus allowing an automated operation of the system during the cruise. A series of measurements of ambient and dissolved nitrous oxide and methane followed by two standards was repeated every 100 min.

The theoretical relaxation time τ of the Weiss equilibrator is given by (Weiss et al., 1992)

$$\tau = V_a / (\alpha Q)$$

where V_a stands for the volume of air in the equilibrator (approximately 20 l), Q is the water flow through the equilibrator (23 l min^{-1}), and α is the Ostwald solubility coefficient. Using the mean water temperature during the EGAMES cruise of 23.4 ± 1.7°C and the corresponding Ostwald solubility coefficients (extrapolated from the tables of Wilhelm et al. (1977)) of 0.6209 and 0.0348 for N_2O and CH_4, respectively, typical relaxation times were 1.4 min for N_2O and 25 min for CH_4. Laboratory experiments of Butler et al. (1988) confirmed the response time of nitrous oxide. Since the Weiss equilibrator is vented to atmospheric pressure and the theoretical relaxation time for methane is relatively long compared to the sampling time (5 min with a flow of 25 ml min^{-1}) an uncertainty for the methane concentration in the equilibrator headspace might be introduced by the influx of ambient air. However, we calculated this effect to cause a change in the

headspace concentration of less than 0.6%. Because the precision of our system for atmospheric methane measurement was 2.8% we did not take into account this effect. For further details of the theory and performance of the Weiss equilibrator see Butler et al. (1988) and Weiss et al. (1992). We observed a slight temperature enhancement between the seawater in situ and the water in the equilibrator (0.1 ± 0.9°C). As indicated by the standard deviation of ± 0.9°C the observed temperature enhancement occurred not systematically. Because a continuous temperature monitoring of the equilibrator water was not available, we did not take into account the temperature effect for the solubility calculations. Possibly occurring methane production within the equilibrator was not observed. However, to exclude any influence of methane formation the equilibrator was cleaned frequently. Methane production within the plumbing system of the ship was negligible because of the high water flow which was considerably greater than the flow through the equilibrator.

We used two combined standard gas mixtures of nitrous oxide and methane in synthetic air (315 ppbv N_2O/1.73 ppmv CH_4 (±2%) and 354 ppbv N_2O/3.02 ppmv CH_4 (±2%)) to create a two-point calibration curve for each measurement. The gravimetrically prepared standard gas mixtures have been calibrated by the manufacturer (DEUSTE Steininger GmbH, Mühlhausen, Germany) against standards of the U.S. National Institute of Standards and Technology, Gaithersburg, Maryland, USA). The mean relative error for the atmospheric mixing ratio measurements was 1.9% for N_2O and 2.8% for CH_4. We calculated the mean relative error of the water concentration measurements to be 2.4% for nitrous oxide and 2.8% for methane. The mean relative error of the saturation was 3.4% for N_2O and 4.0% for CH_4.

All meteorological data were obtained from the ship's record. The salinity and the water temperature were measured continuously with a permanently installed conductivity–temperature–depth (CTD) probe (Zülig, Switzerland).

4. Calculations

Saturation values (expressed in %, i.e. 100% = equilibrium) were calculated as the ratio of the dis-

solved gas and the expected equilibrium value derived from the ambient air mixing ratio:

$$Sat = 100 C_w / C_a$$

$$C_{a,w} = \beta x$$

where C is the equilibrium water concentration (mol l^{-1}), β is the Bunsen solubility, x is the dry mole fraction of the gas in the atmosphere or in the headspace of the equilibrator, and a and w refer to the atmosphere and to the water phase, respectively. Water concentrations were calculated with the functions for the Bunsen solubilities given by Weiss and Price (1980) for nitrous oxide and Wiesenburg and Guinasso (1979) for methane. Transfer coefficients (k_w in cm h^{-1}) of the gases were estimated with the well known equations of Liss and Merlivat (1986):

$$k_w = 0.17 u_{10} (600/Sc)^{2/3}, \quad u_{10} \leq 3.6 \text{ m s}^{-1}$$

$$k_w = (2.85 u_{10} - 9.65)(600/Sc)^{1/2},$$

$$3.6 < u_{10} \leq 13 \text{ m s}^{-1}$$

$$k_w = (5.9 u_{10} - 49.3)(600/Sc)^{1/2},$$

$$u_{10} > 13 \text{ m s}^{-1}$$

u_{10} is the actual windspeed at 10 m height, Sc is the Schmidt number of the gas at the actual water temperature and salinity. The windspeed recorded every 30 min at 18 m height was normalized to 10 m height by using a empirical derived equation for the neutral drag coefficient (Garratt, 1977). The Schmidt number defined as ratio of the kinematic viscosity of seawater to the diffusion coefficient of the gas were calculated with the equations for the kinematic viscosity cited in Siedler and Peters (1986). The diffusion coefficients were derived from the equation of Jähne et al. (1987) for methane and the values for nitrous oxide given in Broecker and Peng (1974). Flux densities (F in mol m^{-2} s^{-1}) across the seawater–atmosphere interface were calculated with the simple equation:

$$F = k_w \Delta C = k_w (C_w - C_a)$$

5. Results and discussion

5.1. Nitrous oxide

The atmospheric mixing ratios showed no significant fluctuations from the mean value of 315 ± 6 ppbv. This value is in good agreement with the global nitrous oxide mixing ratio in 1990 of 310 ppbv (Houghton et al., 1990). In Fig. 2 an overview of the nitrous oxide saturation during the cruise is presented. During the cruise the surface waters were always slightly supersaturated with nitrous oxide except in Amvrakikos Bay where we observed undersaturation at one time (Fig. 2). We observed no
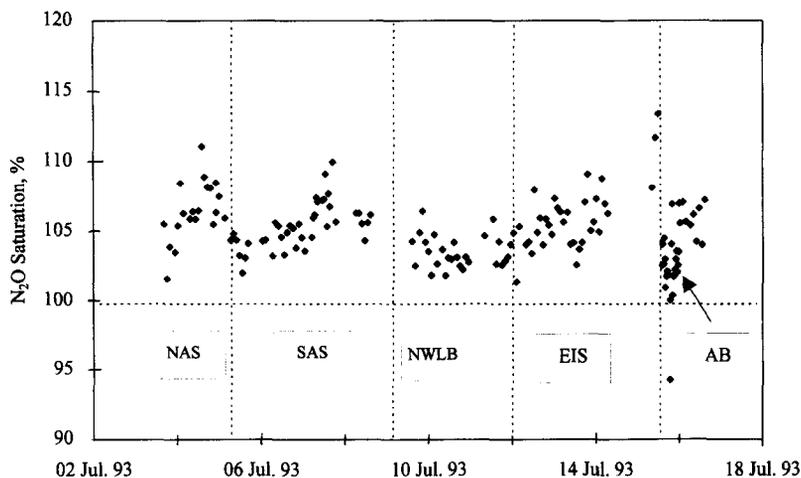
Fig. 2. Overview of the nitrous oxide saturation during the cruise: *NAS* = northern Aegean Sea, *SAS* = southern Aegean Sea, *NWLB* = northwestern Levantine Basin, *EIS* = eastern Ionian Sea, *AB* = Amvrakikos Bay.

Table 1

Results of the nitrous oxide and methane measurements during the EGAMES expedition (arithmetical means $\pm 1\sigma$)

	N_2O			CH_4		
	saturation (%)	water conc. (nmol l^{-1})	flux density (nmol m^{-2} s^{-1})	saturation (%)	water conc. (nmol l^{-1})	flux density (nmol m^{-2} s^{-1})
North Aegean Sea	106 ± 2	7.27 ± 0.07	0.0038	231 ± 32	4.80 ± 0.31	0.018
South Aegean Sea	105 ± 2	6.83 ± 0.27	0.0070	149 ± 18	3.17 ± 0.45	0.022
NW Levantine Basin	104 ± 1	6.54 ± 0.23	0.0206	118 ± 7	2.44 ± 0.16	0.035
Eastern Ionian Sea						
open ocean	105 ± 2	7.02 ± 0.60	0.0210	135 ± 24	2.93 ± 0.74	0.040
shelf	107 ± 3	7.21 ± 0.41	0.0012	148 ± 22	3.19 ± 0.57	0.003
Amvrakikos Bay	103 ± 2	6.55 ± 0.32	0.0028	522 ± 177	11.11 ± 3.84	0.167

significant differences between the mean concentrations in coastally influenced shelf waters (e.g. Samothraki Plateau, Amvrakikos Bay) and the open Aegean Sea, the northwestern Levantine Basin and the eastern Ionian Sea (Table 1). However, the concentrations were slightly variable and might be influenced by regional circulation patterns. For example, in the eastern Ionian Sea we passed the extensions of the Cretan and Pelops gyres (Theocharis et al., 1993) and observed an increase of the nitrous oxide concentration. The saturations of dissolved nitrous oxide in the eastern Ionian Sea are comparable with estimated surface water saturations for two stations lo-

cated in the central and southern Ionian Sea (123% and 142%, respectively) measured by Lavoie et al. (1982) in September 1980. However, Weiss et al. (1992), during a transect across the central Ionian Sea and southern Levantine Basin in December 1977, found considerably lower saturation values in the range of 98–100%. In spite of different hydrographical and biological characteristics between the sampling areas in our study and those of Lavoie et al. (1982) and Weiss et al. (1992) differences in the N_2O saturations of the eastern Mediterranean Sea might be interpreted as the result of a seasonal variability. Similar observations of nitrous oxide su-
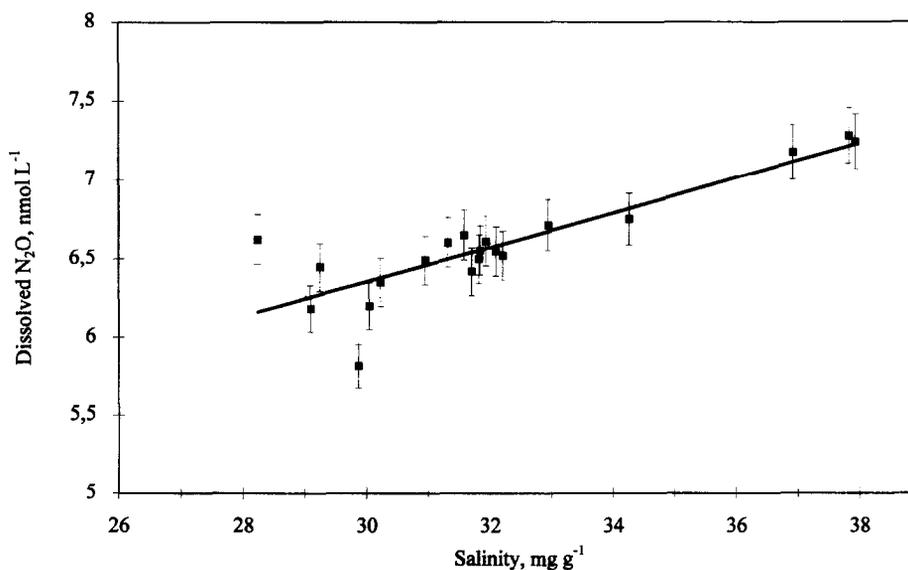
Fig. 3. Nitrous oxide water concentrations in Amvrakikos Bay, $r^2 = 0.7336$ ($n = 24$).
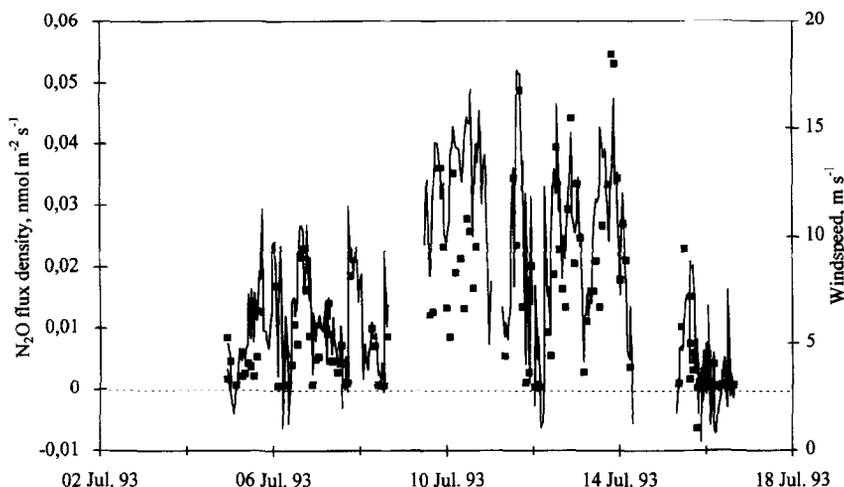
Fig. 4. Flux densities of nitrous oxide across the water–atmosphere interface. (The solid line represents the windspeed.)

persaturation in summer and undersaturation in win ter were also reported for the Baltic Sea (Bange et al., 1995) and Greenland Sea (Weiss et al., 1992).

Both measurements in the North Sea (Law and Owens, 1990; Bange, 1994) and the Baltic Sea (Bange et al., 1995) support our observations in the Aegean Sea, indicating that the mean saturations of dissolved nitrous oxide in shelf areas do not differ from the open ocean. During our stay in the Amvrakikos Bay estuary, we observed a salinity gradient from 37‰ at the mouth to 27‰ in the bay and a positive correlation of salinity with dissolved nitrous oxide (Fig. 3). This pronounced positive correlation is in contrast to measurements in other estuarine systems which showed increasing water concentrations of dissolved nitrous oxide along a decreasing salinity gradient (Butler et al., 1987; Bange et al., 1992; Law et al., 1992). Production in the sediments is assumed to be the main source of estuarine nitrous oxide (Seitzinger et al., 1983; Law et al., 1992). However, the shape of the profile of dissolved nitrous oxide in Amvrakikos Bay might be the result of mixing and/or removal processes rather than production in the sediments.

In view of the hydrographic conditions of the Aegean Sea, we calculated separate mean saturations values of both gases for the northern and southern Aegean Sea, the eastern Ionian Sea, the northwestern Levantine Basin, and Amvrakikos Bay (Table 1). The mean saturation values for the three regions do not differ very much, thus indicating that nitrous oxide was homogeneously distributed in the surface waters of the whole study area. The overall mean saturation value for the cruise was $105 \pm 2\%$. This value is in good agreement with the observation that most parts of the world's ocean surface waters are close to equilibrium showing a mean saturation of about 103% (Weiss, 1978; Butler et al., 1989). Because the saturation values in the Aegean Sea and the surrounding areas were almost uniform, the resulting flux densities were controlled mainly by the variation of windspeed, which ranged from 0.4 m s^{-1} to 18 m s^{-1} (Fig. 4). The mean flux density across the ocean–atmosphere interface was calculated to be 0.012 ± 0.013 nmol m^{-2} s^{-1} yielding an emission flux of 3.0×10^6 kg N_2O yr^{-1} for the Aegean Sea.

6. Methane

The atmospheric mixing ratios showed no significant variations and a mean value of 1.88 ± 0.07 ppmv. This value is in agreement with the results of a recent analysis of the tropospheric methane mixing ratios by Khalil et al. (1993). Fig. 5 shows the curve of the concentration of dissolved methane during the cruise. The water concentrations vary considerably due to the various hydrographic regions of the Aegean Sea and the adjacent areas. We observed the highest
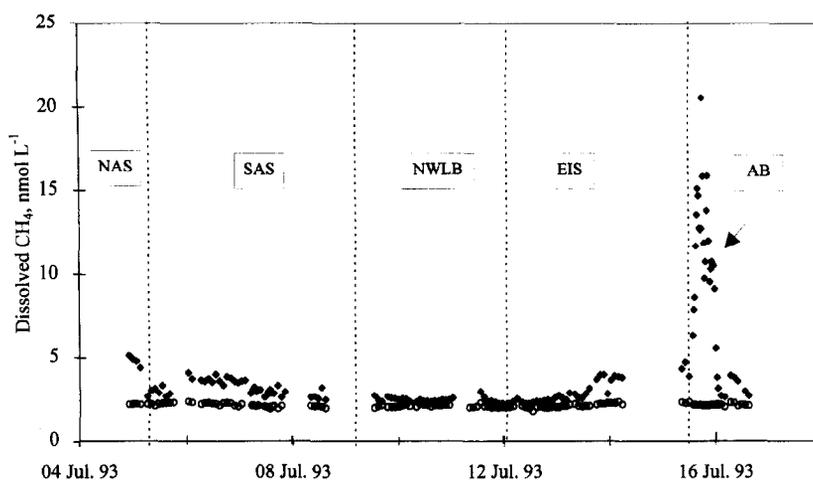
Fig. 5. Methane water concentrations (diamonds) and the theoretical equilibrium water concentrations (circles) calculated with the ambient atmospheric mixing ratios: NAS = northern Aegean Sea, SAS = southern Aegean Sea, NWLB = northwestern Levantine Basin, EIS = eastern Ionian Sea, AB = Amvrakikos Bay.

values in Amvrakikos Bay and the lowest in the northwestern Levantine Basin. Comparable to our nitrous oxide observations, we measured increasing methane concentrations when we passed the extensions of the Cretan and Pelops gyres in the eastern Ionian Sea (Fig. 5). The overall distribution of dissolved methane is reflected by the mean saturation values for the different regions (Table 1). The lowest mean saturation was calculated for the northwestern Levantine Basin ($118 \pm 7\%$), whereas our measurements in Amvrakikos Bay yielded a mean saturation

of about $522 \pm 177\%$. Significantly elevated saturation values were also observed in the northern Aegean Sea ($231 \pm 32\%$). The methane saturation distribution in the Aegean Sea is obviously influenced by the hydrographic and biological characteristics of the sampled areas. The relatively high methane content of the northern Aegean Sea (i.e. the Samothraki Plateau) might be explained by the influence of inflowing Black Sea waters which are highly supersaturated with methane (2–5 times solubility equilibrium with the atmosphere) (Reeburgh et al., 1991). A
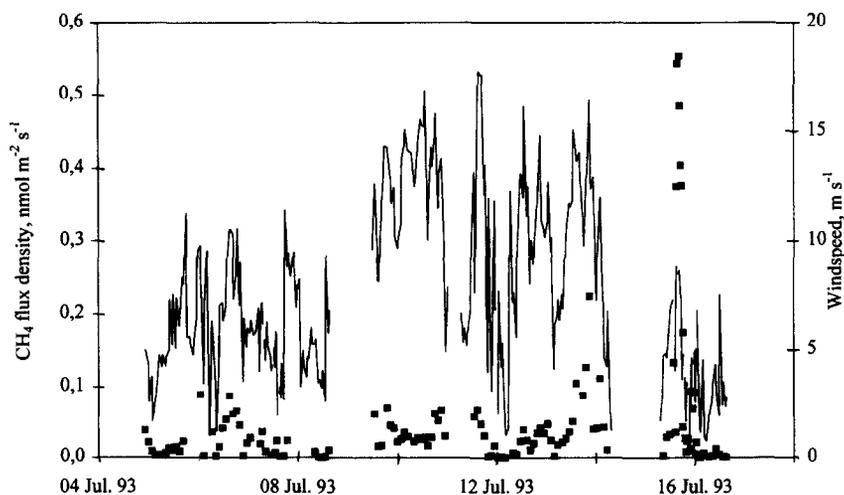
Fig. 6. Flux densities of methane across the water–atmosphere interface. (The solid line represents the windspeed.)

pronounced change in the salinity from 28‰ (Samothraki Plateau) to 37‰ (open Aegean Sea) marked the occurrence of water masses from different origins and support the view that during our cruise the northern Aegean Sea was influenced by Black Sea waters (Theocharis and Georgopoulos, 1993).

Estuaries generally show extreme saturation values because of the high sedimentary production rates of methane. Recent measurements in estuarine systems yielded saturation values up to 11,000% (de Angelis and Scranton, 1993; Scranton et al., 1993) and are comparable with our observations in Amvrakikos Bay. The saturation differences between the southern Aegean Sea, the eastern Ionian Sea and the northwestern Levantine Basin could be the result of distinct coastal influences indicating that the oligotrophic Levantine Basin is less influenced by methane-enriched coastal waters than the others. However, our measurements are in agreement with saturation values of about 130 and 135% which we estimated from reported methane surface water concentrations of two stations in the central and southern Ionian Sea (Lavoie et al., 1982). Assuming that the northern part of the Aegean Sea represents approximately a third of the total area of the Aegean Sea we calculated an area-weighted mean saturation value of 176 ± 16%.

The calculated methane flux densities are shown in Fig. 6 together with the windspeed. It is obvious that the flux densities are mainly controlled by the windspeed except in Amvrakikos Bay, where the flux densities are clearly dominated by the high supersaturations. Based on an area-weighted flux density for the northern and the southern Aegean Sea $(0.021 \text{ nmol m}^{-2} \text{ s}^{-1})$ we estimated the oceanic flux of methane to the atmosphere to be 1.9×10^6 kg $CH_4 \text{ yr}^{-1}$.

7. Summary

Atmospheric mixing ratios of both nitrous oxide and methane remained nearly constant. The two gases showed considerable differences in the saturation distribution in the surface waters of the Aegean Sea and the adjacent areas. This observation might be explained by their different production mecha-

nisms. The mean saturation of nitrous oxide was 105 ± 2% with no significant differences between shelf areas and the open ocean areas. Our measurements in the estuarine system of Amvrakikos Bay showed unexpectedly low water concentrations of nitrous oxide, whereas the methane water concentrations reached maximum values. The mean methane saturations ranged from 118 ± 7% in the oligotrophic northwestern Levantine Basin to about 522 ± 177% in the Amvrakikos Bay estuary. We concluded that in the northern Aegean Sea the inflowing methane-enriched waters from the Black Sea might be the reason for an enhanced mean saturation of 231 ± 32%. Since both gases were supersaturated in the surface waters, the Aegean Sea and the adjacent areas were sources of nitrous oxide and methane in the summer of 1993. However, our emission estimates did not consider that the emission fluxes are influenced by seasonal variations of hydrographic (e.g., sea surface temperature, mixed layer depth), biological (methanogenesis, denitrification/nitrification processes), and meteorological (windspeed) parameters, thus indicating that the air–sea fluxes might be lower during winter time. Nevertheless, the saturation distributions of nitrous oxide and methane in the Aegean Sea reflect at a small scale all characteristic patterns of observations worldwide and therefore further investigations of trace gases fluxes in the Aegean Sea appear to be worthwhile.

Acknowledgements

References

Bange, H.W., 1994. Messungen von Lachgas (N$_2$O) und Methan (CH$_4$) in europäischen Nebenmeeren. Ph.D. thesis, Mainz University.
Bange, H.W., Rapsomanikis, S. and Andreae, M.O., 1992. The

contribution of coastal and shelf areas to the marine emissions of N$_2$O: Measurements of dissolved and atmospheric N$_2$O in the Gironde estuary. Ann. Geophys., 10, Suppl. II: C 221.

Bange, H.W., Bartell, U.H., Rapsomanikis, S. and Andreae, M.O., 1994. Methane in the Baltic Sea and North Seas and a reassessment of the marine emissions of methane. Global Biogeochem. Cycles, 8: 465–480.

Bange, H.W., Rapsomanikis, S. and Andreae, M.O., 1995. Nitrous oxide in the Baltic Sea: Measurements and a model of the seasonal variability. Tellus, submitted.

Broecker, W.S. and Peng, T.-H., 1974. Gas exchange rates between air and sea. Tellus, 26: 21–35.

Butler, J.H., Jones, R.D., Garber, J.H. and Gordon, L.I., 1987. Seasonal distribution and turnover of reduced trace gases and hydroxylamine in Yaquina Bay, Oregon. Geochim. Cosmochim. Acta, 51: 697–706.

Butler, J.H., Elkins, J.H., Brunson, C.M., Egan, K.B., Thompson, T.M., Conway, T.J. and Hall, B.D., 1988. Trace gases in and over the West Pacific and East Indian Oceans during the El Niño-Southern Oscillation event of 1987. Natl. Oceanic and Atmospheric Administration Data Report ERL ARL-16, Air Resources Laboratory, Silver Spring, Maryland.

Butler, J.H., Elkins, J.W., Thompson, T.M. and Egan, K.B., 1989. Tropospheric and dissolved N$_2$O of the West Pacific and Indian Oceans during the El Niño Southern Oscillation Event of 1987. J. Geophys. Res., 94: 14,865–14,877.

Cicerone, R.J. and Oremland, R.S., 1988. Biogeochemical aspects of atmospheric methane. Global Biogeochem. Cycles, 2: 299–327.

Crutzen, P.J. and Schmailzl, U., 1983. Chemical budgets of the stratosphere. Planet. Space Sci., 31: 1009–1032.

de Angelis, M.A. and Scranton, M.I., 1993. Fate of methane in the Hudson River and Estuary. Global Biogeochem. Cycles, 7: 509–523.

Garratt, J.R., 1977. Review of the drag coefficients over oceans and continents. Mon. Weather Rev., 105: 915–929.

Houghton, J.T., Jenkins, G.J. and Ephraums, J.J., 1990. Climate Change: The IPCC Scientific Assessment. Cambridge University Press, Cambridge, 365 pp.

Jähne, B., Heinz, G. and Dietrich, W., 1987. Measurements of the diffusion coefficients of sparingly soluble gases in water. J. Geophys. Res., 92: 10,767–10,776.

Khalil, M.A.K. and Rasmussen, R.A., 1992. The global sources of nitrous oxide. J. Geophys. Res., 97: 14,651–14,660.

Khalil, M.A.K., Rasmussen, R.A. and Moraes, F., 1993. Atmospheric methane at Cape Meares: Analysis of a high-resolution data base and its environmental implications. J. Geophys. Res., 98: 14,753–14,770.

Lashof, D.A. and Ahuja, D., 1990. Relative contributions of greenhouse gas emissions to the global warming. Nature, 344: 529–531.

Lavoie, D.M., Reid, D.F., DePalma, I.P. and Hayes, J.D., 1982. Chemical, biological, and physical measurements from the Mediterranean Sea, summer 1980. NORDA Technical Note

138, Naval Ocean Research and Development Activity, Mississippi.

Law, C.S. and Owens, N.J.P., 1990. Denitrification and nitrous oxide in the North Sea. Neth. J. Sea Res., 25: 65–74.

Law, C.S., Rees, A.P. and Owens, N.J.P., 1992. Nitrous oxide: Estuarine sources and atmospheric flux. Est. Coastal Shelf Sci., 35: 301–314.

Lelieveld, J., Crutzen, P.J. and Brühl, C., 1993. Climate effects of atmospheric methane. Chemosphere, 26: 739–768.

Liss, P.S. and Merlivat, L., 1986. Air–sea exchange rates: Introduction and synthesis. In: P. Buat-Ménard (Editor), The Role of Air–Sea Exchange in Geochemical Cycling. Reidel, Dordrecht, pp. 113–127.

Reeburgh, W.S., Ward, B.B., Whalen, S.C., Sandbeck, K.A., Kilpatrick, K.A. and Kerkhof, L.J., 1991. Black Sea methane geochemistry. Deep-Sea Res., 38: S1189–S1210.

The POEM group, 1992. General circulation of the Eastern Mediterranean Sea. Earth-Sci. Rev., 32: 285–309.

Scranton, M.I., Crill, P., de Angelis, M., Donaghay, P.L. and Sieburth, J.M., 1993. The importance of episodic events in controlling the flux of methane from an anoxic basin. Global Biogeochem. Cycles, 7: 491–507.

Seitzinger, S.P., Pilson, M.E.Q. and Nixon, S.W., 1983. Nitrous oxide production in nearshore marine sediments. Science, 222: 1244–1246.

Siedler, G. and Peters, H., 1986. Properties of seawater. In: J. Sündermann (Editor), Oceanography, Landolt–Börnstein, New Series, Group V, Vol. 3a. Springer, Berlin, pp. 233–264.

Theocharis, A. and Georgopoulos, D., 1993. Dense water formation over the Samothraki and Limnos Plateaux in the north Aegean Sea (eastern Mediterranean Sea). Continental Shelf Res., 13: 919–939.

Theocharis, A., Georgopoulos, D., Lascaratos, A. and Nittis, K., 1993. Water masses and circulation in the central region of the Eastern Mediterranean: Eastern Ionian, South Aegean and Northwest Levantine, 1986–1987. In: A.R. Robinson and P. Malanotte-Rizolli (Editors), Physical Oceanography of the Eastern Mediterranean Sea. Deep-Sea Res., II, 40: 1121–1142.

Weiss, R.F., 1978. Nitrous oxide in the surface water and marine atmosphere of the North Atlantic and Indian Oceans. EOS, Trans. Am. Geophys. Union, 59: 1101–1102.

Weiss, R.F. and Price, B.A., 1980. Nitrous oxide solubility in water and seawater. Mar. Chem., 8: 347–359.

Weiss, R.F., Van Woy, F.A. and Salameh, P.K., 1992. Surface water and atmospheric carbon dioxide and nitrous oxide observations by shipboard automated gas chromatography: results from expeditions between 1977 and 1990. Report No. SIO 92-11, ORNL/CDIAC-59, NDP-044, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Wiesenburg, D.A. and Guinasso, N.L., Jr., 1979. Equilibrium solubilities of methane, carbon monoxide, hydrogen in water and seawater. J. Chem. Eng. Data, 24: 356–360.

Wilhelm, E., Battino, R. and Wilcock, R.J., 1977. Low pressure solubility of gases in liquid water. Chem. Rev., 77: 219–262.