

An improved head-space analysis method for methane in seawater

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Abstract

A widely used degassing method for methane in seawater employing vacuum was tested and subsequently improved. It yielded $62 \pm 3.8\%$ of the total dissolved methane, hence a reproducible correction factor was established. The method was then applied to measure CH_4 in the sea–air boundary layer and simultaneously in the overlying air along two transects in the eastern Equatorial Pacific off Peru in March of 1992. The results showed surprising small-scale reversals of the methane exchange between ocean and atmosphere in this region. Generally the ocean acted as a source of methane but also methane uptake by the ocean was found. This was mainly a consequence of high CH_4 concentrations in the air which deviated considerably from the long-term and large-scale average. If applied to the flux rate calculations, the observed variabilities indicate that both rate and direction of the methane flux through the air–sea interface vary considerably depending on the atmospheric CH_4 content. The implications are that even ocean areas with high concentrations of dissolved CH_4 can be considerably weaker sources than would be expected on the basis of 1.7 ppmv mean atmospheric methane content. Based on improved simultaneous analyses of both air and water samples, the ocean–atmosphere flux of methane would therefore be more dynamic than previously thought.

1. Introduction

Since methane, an important component in the atmospheric inventory of greenhouse gases, is known to be increasing at an average rate of 1%/yr (Blake and Rowland, 1988; Steele et al., 1992), enormous efforts are being made to estimate the contributions from terrestrial sources to the global CH_4 -budget (Rasmussen and Khalil, 1981a,b; Cicerone and Oremland, 1988). However, even today, the role of the oceans and continental shelves remains unclear because of insufficient data and the lack of continuous methane monitoring. Owens et al. (1991) concluded, based on a large set of CH_4 measurements in near-surface waters, that the Arabian Sea is a source for marine methane due to high microbial productivity. The

calculated supersaturations of methane in these surface waters were based on an average atmospheric CH_4 concentration of 1.72 ppmv that was assumed to persist throughout the whole year. However, atmospheric methane concentrations and wind velocities which determine the supersaturation and control the air–sea gas exchange, may be much more variable than presently considered. Highly accurate simultaneous measurements of methane in both air and seawater are needed to exclude these uncertainties and to decide whether certain regions of the oceans act as sources or even as sinks of atmospheric methane.

While gas-chromatography is commonly accepted for the analysis of dissolved gases (Swinnerton et al., 1962), a variety of methods for gas extraction from seawater are being used

(Namiésnik et al., 1990), none of which has reached acceptance as a standard technique so far. Inasmuch as the inventory and dynamics of non-conservative trace gases in the oceans are gaining growing attention, the accuracy and procedure of measurements demand careful standardization. In the case of methane, this is simply determined by the quality of CH₄-standard solutions in seawater. We describe an improvement of a procedure based on the combined vacuum-ultrasonication technique of Schmitt et al. (1991) which can readily be used on board ship to accurately and reproducibly determine the dissolved CH₄ content in large numbers of discrete water samples.

Two basic techniques are commonly used for the extraction of dissolved CH₄ from water samples: the stripping method and the head-space method. The stripping method uses an inert gas (preferably He) to “strip” the sample and to adsorb the gases in a cold trap (Swinnerton and Linnenbom, 1967). Although time consuming and requiring considerable amounts of expensive stripping gas, this method has the advantage of approaching quantitative extraction of dissolved gases. The head-space method utilizes the concept of equilibrium solubilities to calculate the total dissolved fraction of a gas from the equilibrated concentration in the overlying gas phase. This technique allows a simple determination of methane in seawater under most shipboard conditions, but is more time consuming and less accurate at low CH₄ levels. This technique requires also a calibration based on the solubility of methane in seawater and knowledge of the physical conditions which govern equilibration at the time of measurement. A widely and successfully used method for continuous measurements of methane and other gases described by Butler et al. (1988) is based on the equilibration between sprayed seawater and a flowing carrier gas and is therefore well-suited for surface waters but requires large volumes of seawater.

A degassing technique also suitable for deep water samples was introduced by Schmitt et al. (1991) and has since been used under the assumption that it yields total methane in seawater. Our experience with this method revealed a recovery of less than 70% of the total dissolved

CH₄ fraction; hence it is actually a modified head-space method which requires careful calibration.

2. Method and procedure

2.1 Setup

The procedure is referred to as vacuum-ultrasonic method (“VUS”). The water degassing line is schematically shown in Fig. 1 and consists of a graduated 1.15 l sample bottle mounted inside an ultrasonic bath and with removable valve-connections to a gas-burette (*D*) and a water reservoir bottle (*B*). The top of the burette is equipped with a septum port and a gas sample bulb (“gas-mouse”). A third bottle (*C*) which is connected to a vacuum pump, serves as a vacuum-manifold and as a trap for excess water.

2.2 Sampling

The water sampling unit consists of the sample bottle (*A*) with valves *V1* and *V3* attached to it. For sampling, the unit is removed from the degassing system and the valves are closed to prevent contamination. As needed, an appropriate number of these sampling units is prepared and the sampling is carried out directly from the Niskin rosette immediately after recovery.

2.3 Gas extraction

The sampling unit is tightly connected to the degassing line, *V2* is closed and vacuum is applied to the system by opening *V6*. The valves *V5*, *V4* and *V3* are opened and a vacuum is generated in the sample bottle by lowering the water level until the vacuum applied by the pump (≤ 20 mbar) balances the negative pressure of the head-space in the sample bottle. At this point as the level ceases to be lowered, *V3* is closed and the remaining sample volume is noted as that actually being degassed (cf. Table 1).

The dissolved gases are now driven out by ultrasonic energy, alternating (5 s on, 10 s off) for about 5 min which does not affect the temperature of the water bath (20°C). Because the gas reduces the

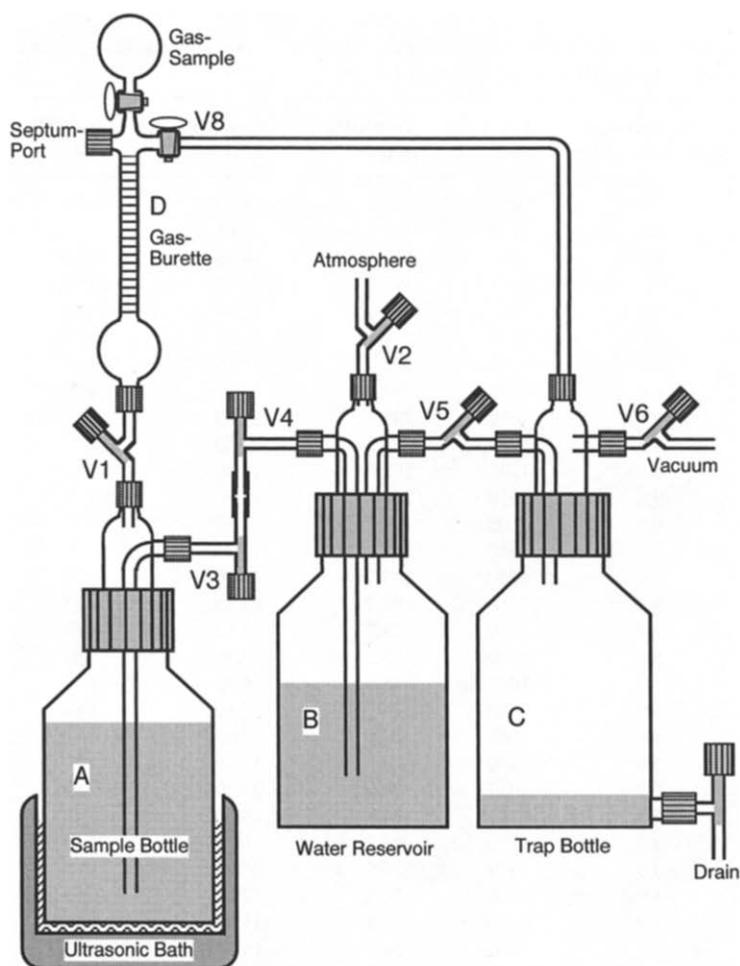


Fig. 1. Schematic setup of the VUS-degassing system after Schmitt et al. (1991).

vacuum and thus the degassing effect, the water level has to be lowered a second time by opening valve *V3* again, until the head-space volume is adjusted to about 250–300 ml (corresponding to 850–900 ml of sample volume) to achieve a sufficiently strong vacuum. Again, alternating ultrasonic energy is applied for 5 min until no more gas is released from the water.

After degassing, the valve *V5* is closed and *V8* is opened for about 30 s to evacuate the burette. By opening the valves *V2*, *V4* and *V3* the extracted gas in the head-space is compressed by being exposed to atmospheric pressure and the volume reduction is compensated by the water from the reservoir bottle (*B*). The extracted gas volume is now

trapped in the head-space of the sample bottle and the valve *V1* is carefully opened to guide the gas into the burette where the volume can be determined and samples of the gas can be taken through the septum for analyses.

The concentration of methane dissolved in the water sample can be calculated based on the analysis of an aliquot of gas by:

$$C = \frac{R \cdot V}{W} \frac{273.15}{273.15 + T_{\text{inj}}} \cdot F_c \quad (1)$$

where *C* is methane concentration in the water (nM), *R* is reading of the gas-chromatograph (μM), *V* is extracted gas volume (ml), *W* is volume of the degassed water (l), *T_{inj}* is analysis

Table 1

Calibration data of the vacuum–ultrasonic degassing method (VUS). Six replicates were run for each of the five concentrations while background values were corrected by iteration of the efficiency factor

Inj.-CH ₄ ^a (nmol/1.15l)	Zero-CH ₄ ^b (nmol/1.15l)	Zero-Corr. ^c (nmol/1.15l)	Eff. Vol. ^d (ml)	True CH ₄ ^e (nM)	Gas-Vol. ^f (ml)	Gas-CH ₄ ^g (μ M)	Yield ^h (nM)	Factor ⁱ
446.8	6.1	9.8	1050	397.1	15.80	15.64	235.3	1.69
446.8	6.1	9.8	1050	397.1	16.60	15.19	240.2	1.65
446.8	6.1	9.8	1000	397.1	18.20	13.85	252.1	1.58
446.8	6.1	9.8	1070	397.1	16.30	16.67	253.9	1.56
446.8	6.1	9.8	1070	397.1	15.90	15.91	236.4	1.68
446.8	6.1	9.8	1100	397.1	16.20	17.34	255.3	1.56
223.4	6.1	9.8	1000	202.8	15.00	8.27	124.0	1.64
223.4	6.1	9.8	1050	202.8	14.90	8.49	120.5	1.68
223.4	6.1	9.8	1050	202.8	13.80	9.16	120.4	1.68
223.4	6.1	9.8	1060	202.8	16.20	8.27	126.3	1.61
223.4	6.1	9.8	1100	202.8	15.60	8.85	125.5	1.62
223.4	6.1	9.8	1070	202.8	14.70	9.29	127.7	1.59
111.7	6.1	9.8	1100	105.7	16.80	4.47	68.2	1.55
111.7	6.1	9.8	1080	105.7	15.00	4.69	65.2	1.62
111.7	6.1	9.8	1050	105.7	19.50	3.57	66.4	1.59
111.7	6.1	9.8	1050	105.7	15.70	4.16	62.1	1.70
111.7	6.1	9.8	1030	105.7	13.60	4.69	61.9	1.71
111.7	6.1	9.8	1090	105.7	17.40	4.02	64.2	1.65
44.7	3.6	5.9	1040	44.0	16.30	1.74	27.3	1.61
44.7	3.6	5.9	1080	44.0	16.60	1.88	28.8	1.52
44.7	3.6	5.9	1060	44.0	17.00	1.79	28.7	1.53
44.7	3.6	5.9	1040	44.0	15.50	1.79	26.6	1.65
44.7	3.6	5.9	1030	44.0	15.20	1.88	27.7	1.59
44.7	3.6	5.9	1100	44.0	13.90	2.14	27.1	1.62
22.3	3.6	5.9	1100	24.5	16.90	1.03	15.8	1.55
22.3	3.6	5.9	1070	24.5	16.70	1.03	16.0	1.53
22.3	3.6	5.9	1040	24.5	17.00	0.98	16.1	1.53
22.3	3.6	5.9	1050	24.5	15.00	1.03	14.7	1.67
22.3	3.6	5.9	1050	24.5	15.50	1.03	15.2	1.62
22.3	3.6	5.9	1080	24.5	14.30	1.12	14.8	1.66

Average efficiency factor = 1.61

Standard deviation $\sigma = 0.056$

^aMethane (nmol/1.15l) added to the seawater volume of 1150 ml; amounts were adjusted from two commercial standards containing 20 μ l and 2000 nl of CH₄ per ml total gas.

^bBackground methane content (nmol/1.15l) in the seawater used in this experiment; the background is based on the uncorrected VUS-method and assumes that all methane is in the gas phase.

^cTrue methane background (nmol/1.15l), as calculated from the uncorrected background by iteration of the resulting average efficiency of the method.

^dEffective sample volume (ml) under vacuum prior to ultrasonic treatment; this volume is assumed to be the water that is actually degassed.

^eTrue methane concentration (nM) in the sample, consisting of the injected amount of CH₄ plus background.

^fVolume (ml) of the total gas recovered.

^gMethane content in nmol per ml aliquot of the recovered gas, as determined by GC analysis.

^hMethane yield (nM) of the vacuum–ultrasonic method, calculated from Eq. (1) with $F_c = 1$. A temperature correction of the gas volume was not applied because the lab temperature was kept constant by air conditioning.

ⁱRatio between the true methane concentration the VUS-method yield. The average value over the whole calibration given in the last line is referred to as the efficiency factor.

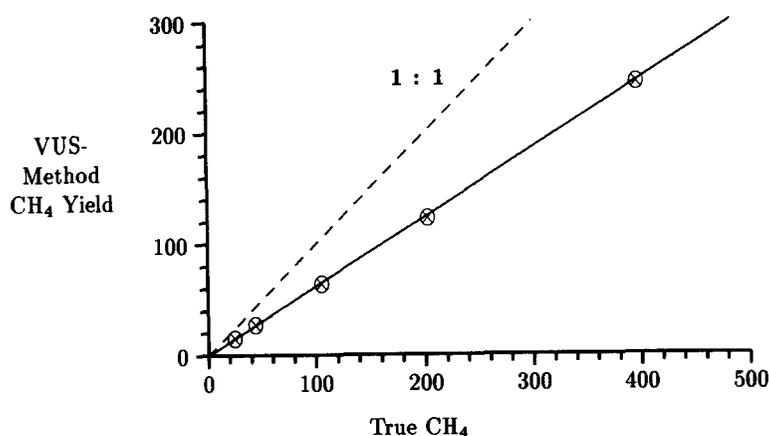


Fig. 2. Correlation between "true" methane concentration in seawater and methane yield of the vacuum/ultrasonic (VUS) method (in μM) (cf. Table 1). The ratio between recovered (gaseous) and residual (dissolved) methane is controlled by the physical conditions of the degassing and not related to the methane concentrations. For constant conditions as used in all subsequent determinations, the mean correction factor is 1.61 ± 0.1 .

temperature of the gas ($^{\circ}\text{C}$), and F_c is efficiency factor of 1.61, according to calibration.

In the case of methane, the aliquot is injected onto a gas-chromatographic column and measured with a flame ionization detector. For this work, a Shimadzu GC 14A FID-GC was used with a Porapak packed column and nitrogen as carrier gas. The methane content is expressed as nmol CH_4 per ml of head-space gas. The temperature correction of the gas volume applies when laboratory temperatures change drastically at the time of GC-analyses.

2.4 Calibration

Known amounts of methane in pure nitrogen were injected into sample bottles filled with HgCl_2 -poisoned seawater (total volume 1150 ml) and allowed to equilibrate for 24 h. Very small volumes (100–500 μl) were injected in order to dissolve a maximum amount of methane in the aqueous phase and in fact, total dissolution of the injected gas was observed in most of the samples through disappearance of all gas phases.

Six replicate samples and one seawater blank for each standard concentration were analysed using the VUS-technique and evaluated as described above. The efficiency factor of the method was approximated in a first step as the ratio between

the method yields and the known standard concentrations. In the following steps, the seawater blanks were iteratively corrected by the previous factors until finally, constant efficiency factors were calculated. This procedure was necessary because the standards were prepared from two different seawater samples and therefore, a standard addition was not applicable.

The calibration data are listed in Table 1 and the results are plotted in Fig. 2. The average final ratios between the "true" methane concentrations and the yields of the VUS-degassing method were found to be 1.61 over the whole range of the calibration. As shown in Table 2, the results of the method corrected by this factor deviate symmetrically from the "true" values by less than 6%.

Under the conditions described here, the VUS-method yields only 62% of the total dissolved methane, therefore we consider it a modified "head-space" method, rather than a "total yield" method. The decompression of the head-space is used to generate an undersaturated gaseous phase and the ultrasonic energy is applied to induce the formation of micro-bubbles and thus to speed up the exsolution. The upper limit of methane concentration in the head-space is given by the equilibrium and the relation between the volumes of gaseous and liquid phase in the vessel:

$$M_t = M_g + M_l = V_g C_g + \alpha V_l C_g \quad (2)$$

Table 2
Reproducibility of methane concentrations in the calibration runs

True CH ₄ (nM)	Corr.CH ₄ (nM)	ΔCH ₄ (nM)	ΔCH ₄ (%)
397.1	378.9	-18.2	-4.6
397.1	386.7	-10.4	-2.6
397.1	405.9	8.8	2.2
397.1	408.8	11.7	2.9
397.1	380.6	-16.5	-4.2
397.1	411.1	14.0	3.5
202.8	199.6	-3.2	-1.6
202.8	194.0	-8.9	-4.4
202.8	193.8	-9.0	-4.4
202.8	203.4	0.6	0.3
202.8	202.0	-0.8	-0.4
202.8	205.6	2.7	1.3
105.7	109.9	4.2	3.9
105.7	104.9	-0.8	-0.7
105.7	106.9	1.2	1.1
105.7	100.0	-5.7	-5.4
105.7	99.7	-6.0	-5.6
105.7	103.4	-2.3	-2.2
44.0	44.0	0.0	0.0
44.0	46.4	2.5	5.7
44.0	46.1	2.2	5.0
44.0	42.9	-1.1	-2.4
44.0	44.6	0.6	1.4
44.0	43.6	-0.3	-0.7
24.5	25.4	0.9	3.5
24.5	25.8	1.3	5.3
24.5	25.9	1.3	5.5
24.5	23.6	-0.9	-3.6
24.5	24.4	-0.1	-0.4
24.5	23.8	-0.7	-2.9

Values of the corrected analyses (*Corr.CH₄*) are the yields of Table 1 multiplied by the average efficiency factor. These corrected results deviate symmetrically from the "true" values (*True CH₄*) by less than 6%.

where M_t is total methane in the vessel, M_g is CH₄ in the head-space, M_l is CH₄ in the liquid phase, V_g is volume of the head-space, V_l is volume of the liquid phase, C_g is partial pressure of CH₄ in the head-space, and α is the Bunsen coefficient

Table 3 shows equilibration yields of methane calculated from Eq. (2) for different volume relations between head-space and water. It can be seen that for the typical VUS-volumes of 250 ml head-space and 900 ml water ($V_g/V_l = 0.278$), the maximum yield is approximately 91% of the total methane and would increase with the V_g/V_l ratio, e.g. to 97.3% for equal volumes of both phases, respectively. Nevertheless, the expansion of the head-space gas prior to degassing and the re-compression to 1 bar afterwards results in a pre-concentration of the analysed gas. As can be seen in Table 3, a re-compressed head-space of e.g. 15 ml finally collected in the burette is about 300% more concentrated than would be the case at equilibrium between 15 ml head-space and 1135 ml water at 1 bar ($V_g/V_l = 0.013$). A re-resolution of the super-saturated methane in the burette is hampered by the small water surface and hence was found to be negligible for at least 20 min after re-compression.

The constant efficiency difference of 29% indicates that the VUS-degassing which is induced and accelerated by the ultrasonic energy, is not related to equilibration and determined by physical effects as, for example, by the generation of micro-bubbles. Continuous ultrasonication over 10 min was occasionally observed to cause increasing standard deviations of multiple measurements by about 4% which is possibly a cracking effect of higher hydrocarbons in solution (Suslick, 1988). A similar effect may be expected for variations of the

Table 3
Methane fractionation between the seawater sample equilibrated head-space for different V_g/V_l ratios calculated after Eq. (2). The Bunsen coefficient at $T = 20^\circ\text{C}$ and $S = 34 \cdot 10^{-3}$ is $\alpha = 0.028$

V_g/V_l	0.01	0.013	0.05	0.1	0.2	0.278	0.5	1.0	2.0
M_g (%)	26.3	32.1	34.7	78.2	87.7	90.8	94.7	97.3	98.6
M_l (%)	73.7	67.9	65.3	21.8	12.3	9.2	5.3	2.7	1.4

M_g = methane gaseous; M_l = methane remaining in liquid.

ultrasonic power. However, an impact of the ultrasonic energy is minimized by the frequent application.

The calibration results confirm that the linear correlation between the recovered gaseous and remaining dissolved methane fraction is not dependent on the concentrations but controlled entirely by the physical parameters of the degassing. The accuracy and reproducibility of the VUS-method therefore depends on constant conditions and operation. This is supported by an intercalibration performed on board the RV *Sonne* 80b expedition (East Pacific Rise) in July/August 1992, where both, VUS- and stripping-method were used for parallel analyses of water samples recovered from hydrothermal plumes (Univ. Hamburg, Inst. Biogeochem. Meereschem., 1993).

In the stripping procedure, water samples were purged with He for about 30 min and the hydrocarbon gases were adsorbed by a cold-trap and Al₂O₃-activated charcoal at –80°C. Afterwards, the traps were heated to 80°C and the desorbed gases were analysed with an FID gas-chromatograph. The total time required for both cycles of the stripping method is 45–50 min, compared to 10–15 min for the VUS-degassing. The comparison between results from both techniques revealed a good linear correlation (> 0.9) but considerable deviations between the absolute values (Univ. Hamburg, Inst. Biogeochem. Meereschem., 1993). Recoveries of multiple VUS-degassings were assumed to represent 100% of the dissolved methane and compared to the yields of single degassings performed as described above. From the *Sonne* 80b measurements, the total yield of the VUS-method is estimated to be 72% and the resulting efficiency factor was used to correlate VUS-technique and the He stripping-method. The latter was assumed to yield 100% of the total dissolved methane. Compared to our results, this indicates that under continued application of vacuum, equilibration gains control and finally approaches the 90% exsolution limit described above.

Careful standard calibration makes the VUS-technique a useful and time-saving method for gas extraction from seawater samples, especially

for the on-board detection of methane plumes in deep-water from hydrothermal venting and cold seeps. However, it offers possibilities for further improvements concerning the total gas yield and the requirements for analyses of other gases in seawater which are not considered in this work. Further implementations, e.g. of spray equilibration as described by Butler et al. (1988), could be combined with the advantages of this technique for the development as a standard extraction of dissolved gases in seawater.

3. Sea–air methane flux

The gas exchange between sea surface and atmosphere generally is a function of the concentration gradient ΔC between both phases:

$$F = k \cdot \Delta C \quad (3)$$

where k is the gas exchange coefficient or “piston velocity” (cm/h). The coefficient k is a function of the specific gas properties, the temperature T (°C) and the wind velocity v (m/s), as described by Wanninkhof (1992):

$$k = 0.31 v^2 \cdot \left(\frac{Sc}{660} \right)^{\frac{1}{2}} \quad (4)$$

The Schmidt number Sc is a function of temperature and is defined as the ratio between the kinematic viscosity of the water and the diffusion coefficient of the gas. For methane in seawater it can be determined by a third-order polynomial according to Wanninkhof (1992):

$$Sc = 2039.2 - 120.31 T + 3.4209 T^2 - 0.040437 T^3 \quad (5)$$

The gas exchange coefficient k can thus be calculated from the water temperature and the wind velocity in the boundary layer by Eqs. (4) and (5). According to Eq. (3), the gas flux through the ocean–air interface also depends upon the CH₄-concentration gradient (ΔC) between both phases, which can be expressed as the difference between the actual gas concentration in the surface water and the theoretical value at equilibrium with the atmosphere. The ratio between the actual CH₄ in the water and the equilibrium concen-

tration is also referred to as the relative saturation of the water.

4. Equilibrium solubility of methane in seawater

The ability of seawater to dissolve a gas is dependent on the pressure, temperature, salinity and the concentration of the gas (partial pressure) in the atmosphere. In principle, the concentration C^* of a dissolved gas can be calculated from the Bunsen solubility coefficient α (at given temperature and salinity) and its atmospheric partial pressure P_G by Henry's law:

$$C^* = \alpha \cdot P_G \quad (6)$$

Since the atmospheric partial pressure of methane varies seasonally and shows considerable regional deviations from the large scale and the long-term average (Rasmussen and Khalil, 1981a; Blake and Rowland, 1988), the amount of methane dissolved in surface seawater has to be expressed as a function of salinity, temperature and the CH_4 mol-fraction in moist air at atmospheric pressure. Wiesenburg and Guinasso (1979) introduced an equation for equilibrium concentrations of several non-conservative atmospheric trace gases in seawater after Weiss (1970) to meet these requirements:

$$\begin{aligned} \ln C^* = \ln f_G + A_1 + A_2 \cdot \left(\frac{100}{T} \right) \\ + A_3 \cdot \ln \left(\frac{T}{100} \right) + A_4 \cdot \left(\frac{T}{100} \right) \\ + S \cdot \left[B_1 + B_2 \cdot \left(\frac{T}{100} \right) + B_3 \cdot \left(\frac{T}{100} \right)^2 \right] \quad (7) \end{aligned}$$

where C^* is equilibrium concentration, f_G is atmospheric mol fraction, T is absolute temperature (K), and S is salinity (10^{-3}).

Eq. (7) applies the Bunsen solubility data for methane by Yamamoto et al. (1976), which cover a wide range of temperatures and salinities. In the case of methane, the constants for the calculation

in nM are:

$$\begin{aligned} A_1 &= -415.2807, \\ A_2 &= 596.8104, \\ A_3 &= 379.2599, \\ A_4 &= -62.0757, \\ B_1 &= -0.05916, \\ B_2 &= 0.032174, \\ B_3 &= -0.0048198. \end{aligned}$$

5. Methane at the air–sea interface in the eastern Equatorial Pacific

5.1 Material and methods

In order to test the method rigorously, seven sets of simultaneous air and water measurements were carried out in the eastern Equatorial Pacific along two transects perpendicular and parallel to the Peruvian coast during RV *Sonne* 78 expedition in March/April 1992 (Suess, 1992) (cf. Fig. 3). Samples were taken from a zodiac at a distance of about half a mile upwind from the ship. Air samples were taken directly above the water surface and sucked into 1 l glas bottles equipped with two vacuum-tight valves by means of a mechanical pump. Water samples were taken in 2 l Niskin samplers just below the sea surface. Analyses were carried out on board immediately after sampling using the above described VUS-degassing system and gas-chromatography.

5.2 Results and discussion

The observed data and the methane flux rates calculated after Wanninkhof (1992) are shown in Table 4 together with the physical parameters that are related to methane solubilities and the degree of saturation. Most surprisingly, these results indicate both, a net flux of methane to the atmosphere at stations 1–4 and a methane flux from the atmosphere at stations 5–7. According to Eqs. (3)–(5), the general direction of the methane flux into or out of the sea surface is determined by the saturation difference between seawater and air which may be assumed less variable over a longer period. On the other hand, the absolute flux rates are strongly

Table 4
Results of simultaneous methane measurements in air and seawater at seven stations off Peru

Station-No.	1	2	3	4	5	6	7
Date	3/11/1992	3/12/1992	3/12/1992	3/15/1992	3/18/1992	3/21/1992	3/26/1992
Latitude (°S)	6°48.47'	5°30.48'	5°31.63'	5°34.87'	6°50.81'	11°04.02'	9°35.36'
Longitude (°W)	88°25.30'	85°22.48'	83°41.80'	81°52.93'	81°26.63'	78°25.55'	80°07.53'
Air-CH ₄ (ppmv)	1.86	1.89	1.92	2.01	2.00	2.01	2.00
Eq. conc. (nM)	1.96	2.00	2.04	2.13	2.11	2.12	2.14
Water-CH ₄ (nmol)	2.6 (1.6)	2.3 (1.4)	2.8 (1.7)	9.2 (5.8)	2.3 (1.4)	2.0 (1.3)	1.8 (1.1)
ΔC (%)	130	115	130	440	110	95	86
ΔC (nM)	0.6 ± 0.1	0.3 ± 0.1	0.7 ± 0.1	7.1 ± 0.3	0.2 ± 0.1	-0.1 ± 0.1	-0.3 ± 0.1
T (°C)	27.4	27.2	27.2	27.3	27.4	27.4	26.8
v (m/s)	7.8	4.5	4.0	3.7	2.8	6.2	4.7
kCH ₄ (cm/h)	21.92	7.29	5.76	4.93	2.82	13.85	7.96
F (mmol/km/d)	3160 ± 500	530 ± 150	970 ± 140	8400 ± 350	140 ± 60	-330 ± 330	570 ± 190

Parameters that are related to CH₄ saturations and flux rates, refer to Eqs. (3)–(5). The equilibrium concentration of CH₄ assuming an atmospheric content of 1.70 ppmv would be 1.8 nM (compare to line 5). Note the difference between the “true” methane concentrations at line 6 the results of the original VUS-method (numbers in brackets). The total errors given for the concentration gradients (ΔC) the methane fluxes (F) refer to ±0.05 ppmv as the precision range of the air measurements ±4% as the estimated error of the VUS-analyses.

influenced by the wind speed and thus subject to short-term variations. However, the observed fluxes appear to reflect more general trends of the two major parameters, i.e. an increase of CH₄ in the air towards the coast and a decrease of CH₄ in the ocean surface in a southern direction along the coastal upwelling zone.

For dissolved methane the same trend was recently found in the surface waters of the Central Pacific between 0° and -5° S (Bates et al., 1993) but due to the much lower atmospheric CH₄ values of 1.6–1.7 ppmv, the reverse concentration gradient induced a positive flux into the atmosphere of about 300 mmol/km²/d (Bates et al., 1993; Matsueda et al., 1993). Matsueda et al. (1993) suggested that the N–S decrease of atmospheric methane in the Central Pacific is related to decreasing marine production towards the south. Khalil and Rasmussen (1986) have shown that significant interannual decreases of atmospheric CH₄ correlated with the intensity of the El Niño Southern Oscillation (ENSO) off Oregon and suggested a lower than normal marine CH₄-production as one possible explanation. Although a moderate ENSO event also occurred during our measurements in March of 1992, our data do not indicate such trends for atmospheric CH₄ along the upwelling zone off Peru, but the N–S decrease of

dissolved CH₄ probably also reflects an ENSO-triggered decrease of marine production. However, mainly the increased air-methane concentrations and low wind velocities inhibited and partly even inverted the methane flux through the water–air interface in this area during March 1992. No conclusions can be drawn as to the duration and the extent of these conditions on the basis of a single set of data. Nevertheless, it illustrates the influence of atmospheric parameters on both direction and rate of methane flux even in areas which are generally assumed as strong sources for atmospheric methane.

From the above we wish to emphasize the importance of simultaneous atmospheric measurements of CH₄ and - what we believe - the more accurate measurements of CH₄ in the surface waters employing the improved VUS-method. It is readily demonstrated based on the data of Table 4 that the magnitude of CH₄-fluxes and even the direction, i.e. into or out of the sea surface, would be totally different, if one were to rely solely on the mean atmospheric CH₄-content of 1.7 ppmv and on the assumption of total gas yield as implied by the original VUS-method (Schmitt et al., 1991). It seems premature to speculate on other causes of the quite surprising find that the highly productive equatorial productivity belt would be a source but

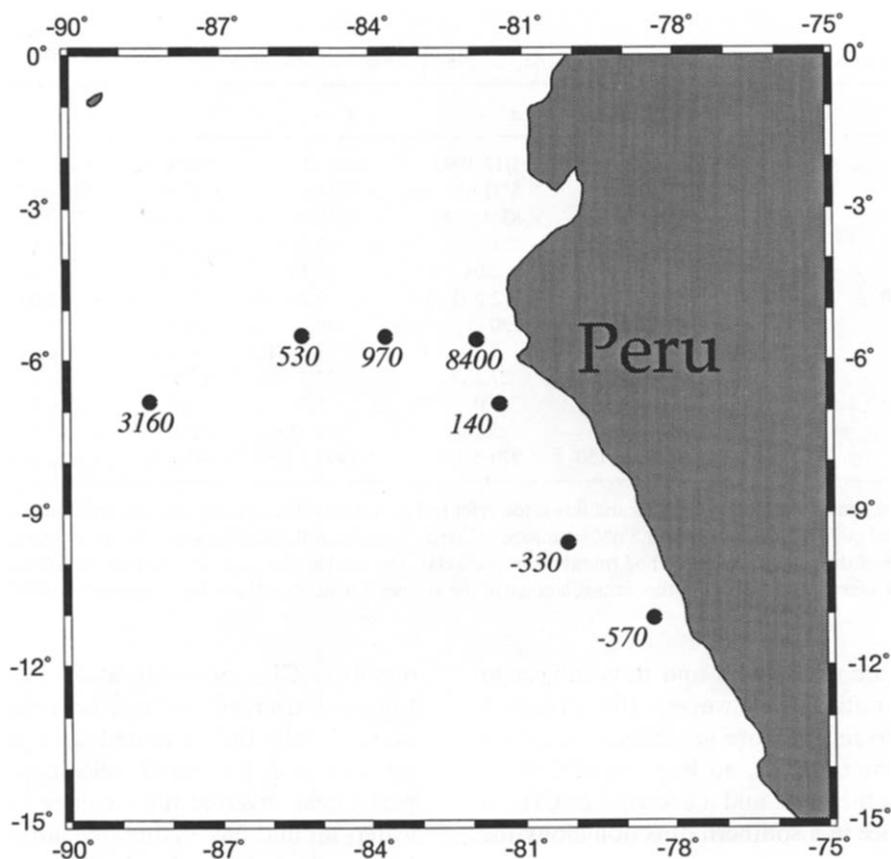


Fig. 3. Map of the sampling area off Peru. Numbers below the station marks denote the methane flux rates ($\text{mmol}/\text{km}^2/\text{d}$) based on the observed saturation gradients between seawater and air (cf. Table 4). Positive values indicate a methane flux from the sea surface into the air and negative values vice versa.

the equally productive coastal upwelling zone off Peru a sink for atmospheric methane. For this discussion, more complete and repeated data sets are needed. Nevertheless, we are convinced that the quality of the data presented here is quite good and that the resulting patchiness of CH_4 exchange is real. These findings demonstrate that the ocean–atmosphere exchange of CH_4 is much more dynamic than thought previously and that the need for more data on the marine CH_4 cycle is even more urgent than stated in the introduction.

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