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Methane flux across the air–water interface: air velocity effects

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ABSTRACT

Methane flux from the air–water interface of freshwater-covered wetland ponds is shown to increase approximately as the square of the air velocity over the water surface. CH_4 fluxes were measured using a partitioned chamber placed over the water surface where the air velocity along the surface can be controlled. Correlating measurements of CH_4 fluxes and surface water dissolved CH_4 concentrations to air velocities provide a means to evaluate the liquid phase exchange coefficient (k_l) for a two-layer model of the gas–liquid interface. The liquid phase exchange coefficient for CH_4 is calculated as $k_l = 1.7$ cm h^{-1} for air velocities of zero and as $k_l = 1.1 + 1.2\ v^{1.96}$ cm h^{-1} for air velocities from 1.4 to 3.5 m s^{-1} and water temperatures of 20 °C. Surface water dissolved CH_4 concentrations of the wetland ponds used in this study varied from 10 to 780 $\mu g\ l^{-1}$, resulting in CH_4 flux measurements from 0.01 to 1.22 g m^{-2} day^{-1}.

1. Introduction

Gas exchange between the atmosphere and supersaturated water of ponds, lakes and bays is a function of the condition of the water surface as well as of the gaseous concentration differences across the air–water interface (Downing and Truesdale, 1955; Kanwisher, 1963). The rate of transfer for O_2 and CO_2 increases with air velocity according to wind tunnel experiments (Hoover and Berkshire, 1969; Liss, 1973), and as indicated by radon transfer rates measured over the ocean (see Deacon, 1981, for a review of previous studies). At low air velocities, gas transfer rates agree with model predictions based on smooth rigid surfaces, but at higher velocities, ripples and waves cause rates of transfer to increase more rapidly suggesting an air velocity power law dependence (Liss and Slater, 1974).

Although extensive measurements of radon transfer rates have been published for a wide range of sea conditions, some uncertainty remains on the interpretation of this data for general application. The radon method requires the effects of horizontal transport to be negligible, and that wind and sea conditions remain constant for a period of about 5 days. Since few measurements are obtained under these stringent conditions, the extent of gas transfer rate increases resulting from wind effects over the ocean remains undetermined (Broecker and Peng, 1974; Peng et al., 1979; Deacon, 1981).

Although global CH_4 input from the ocean to the troposphere is estimated to be low compared to other sources (Liss and Slater, 1974), wetlands, including freshwater and salt water marshes, ponds, flooded-soil agriculture, lakes and bays, are postulated to be major sources of atmospheric CH_4 (Lovelock and Margulis, 1974; Baker-Blocker *et al.*, 1977; Ehhalt and Schmidt, 1978). Starting with an early effort by Conger (1943), many studies have been undertaken to characterize CH_4 emissions from natural sources (Koyama, 1963; Atkinson and Hall, 1976; Martens and Klump, 1980; Cicerone and Shetter, 1981; Harriss and Sebacher, 1981). Most gas flux measurements involved the use of gas-collection chambers placed over an air–water or air–soil interface. Recent advances in chamber system design and operation have significantly increased the quality of data obtained from soil and water surfaces (Matthais et al., 1980; Seiler and Conrad, 1980; Sebacher and Harriss, 1980).

Since the perturbation of air velocity on CH_4 flux from wetland sources adds an uncertainty to global emission estimates, an air velocity controlled chamber was developed to evaluate this effect (Sebacher and Harriss, 1982). This paper presents field data obtained with the new system which demonstrates the effect of changing air velocity on the CH_4 flux across an air–water interface and evaluates the liquid-phase exchange constant for air velocities from 0 to 3.5 m s^{-1}. Measurements were obtained in wetland ponds located in the area of the St. Marks National Wildlife Refuge in Northwest Florida. Seasonal variation of surface water dissolved CH_4 in the pond provided an opportunity to measure CH_4 flux as a function of CH_4 concentration gradient with controlled surface air velocity.

2. Methane flux across the air–water interface

Dissolved gas in an aqueous solution is related to the partial pressure of that gas in the gas phase by Henry's Law:

$$P = HX \tag{1}$$

where P is the partial pressure, X is the mole fraction of gas in solution, and H is Henry's Law constant. The strict application of Henry's Law relates only to equilibrium conditions. In the case where CH_4 is continuously being produced in pond sediments and diffusing through the overlying water to the air, the partial pressure of CH_4 in the water is always above that of the atmosphere. When such a situation exists, the kinetics of exchange of gas between the two phases is assumed to be a steady-state process and is treated as a two-layer boundary system at the air–water interface (Danckwerts, 1970). Various models that can be applied to both mass and heat transfer for random molecular motion in quiescent fluids or in a viscous sub-layer in which there is a gradual transition from molecular to turbulent flow can be found in Kreith (1958), Hinze (1959) and Schlichting (1968).

The two-layer (film) model for non-reacting CH_4 gas exchange across an air–water interface can be written as

$$F = k_l\left(C_l - \frac{c_a}{H}\right) \tag{2}$$

where F is the flux of CH_4 across the interface in mass per area as a function of time, k_l is the exchange coefficient for the liquid phase with dimensions of length per time, H is Henry's Law constant, and C_l and c_a are CH_4 concentrations in mass per volume in the overlying air (a) and dissolved in the water (l) (Liss and Slater, 1974). Although a laminar film of both air and liquid is assumed to exist at the interface, gas exchange between the two phases is controlled by molecular diffusion through the laminar liquid layer. Diffusion in the liquid phase is significantly slower than that in the gas phase, resulting in a CH_4 flux which is rate controlled by the water molecular diffusivity. The exchange coefficient k_l can also be written as

$$k_l = \frac{D}{\delta} \tag{3}$$

where D is the molecular diffusivity of CH_4 in water and δ is the thickness of the liquid laminar layer. Sheer stress resulting from increasing wind velocity tends to tear the laminar layer film and reduce δ. A decreasing δ gives rise to an increasing CH_4 flux across the interface (Liss, 1973).

3. Water temperature effect

Water temperature affects the transfer of dissolved CH_4 through the surface liquid film by its influence on the diffusivity of gas in water and by changes of the viscosity of water. Water viscosity as well as wind stress determine the thickness of the liquid surface layer. In order to account for surface water temperature variations, all CH_4 flux measurements were corrected to 20 °C water temperature by the Schmidt number factor $(Sc_{20}/Sc_T)^{-2/3}$ (Deacon, 1981).

The Schmidt number correction is based on various studies of gas transfer through the surface layer which give k_l proportional to both the frictional velocity in the surface film and Sc raised to the $-2/3$ power (Moller and Schumann, 1970; also see Wesley, 1979, for the heat transfer analog). Since Sc is a ratio of kinematic viscosity (μ) to diffusivity (D) the Schmidt number correction must include the temperature effects on both μ and D. Using the Stokes–Einstein relation that $D\mu/T$ is a constant (T = temperature, deg. K) (Ferrel and Himmelbau, 1967) a relative Schmidt number correction can be obtained in terms of μ and T where $Sc^{-2/3}$ is proportional to $(\mu^2/T)^{-2/3}$.

4. Experimental methods

CH_4 flux across the air–water interface was measured as a function of air velocity, water temperature and surface water dissolved CH_4 with a gas-filter correlation infrared absorption analyzer integrated with a 0.14 m^3 modified chamber (Fig. 1). Details of the CH_4 analyzer design and calibration can be found in Sebacher (1978) and a complete description of the integration system for measuring flux as a function of air velocity is detailed in Sebacher and Harriss (1982). In this system, air is continuously recirculated from the sampling chamber, over the air–water interface, through the CH_4 analyzer and back to the chamber. Any changes in the CH_4 concentration in the chamber are thus continuously monitored. CH_4 flux is calculated directly from the recorded CH_4 concentration change with time since the volume of the chamber and interface area are known. Air velocity is controlled over a range of 0.4 to 3.5 m s^{-1} by a valve incorporated into the blower shown in Fig. 1. For a preset air velocity, the values of flux (F) and air CH_4 concentration (c_a) measured in the chamber are used in eq. (2) to evaluate k_l. All flux measurements were made over water surfaces which were clear of aquatic vegetation.

Surface water dissolved methane concentrations (C_l) were analyzed using liquid stripping gas chromatography (McAuliffee, 1971; Martens and Klump, 1980). Undisturbed water samples were obtained using syringes mounted on a 4 meter pole with a pull-line attached to the syringe plunger. CH_4 flux at zero air velocity was measured with a second chamber which has the same exterior geometry as the primary chamber, but contains no internal partitions or air velocity control system.

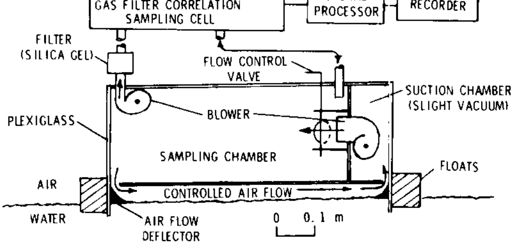

Fig. 1. System used to measure CH_4 flux from the air–water interface as a function of air velocity.

5. Results and discussion

5.1. *Flux measurements versus air velocity*

Measured CH_4 flux across the interface is plotted as a function of air velocity and surface water dissolved CH_4 concentrations in Fig. 2. Surface water temperature data is also shown. When the chamber air velocity was gradually increased, no change in the water surface roughness was detectable until the air velocity exceeded 0.4 m s^{-1}. Above this air velocity the water surface became increasingly rippled to a height of approximately 3 mm at 3.5 m s^{-1}. Fig. 2 shows little change in CH_4 flux values until the air velocity exceeds 0.4 m s^{-1}, but above this air velocity the measurements exhibit a logarithmic characteristic of CH_4 flux across the air–water interface as a function of air velocity.

Chamber air velocities were measured at 2 cm above the water surface with a hot wire anemometer. Correlation of chamber air velocities to actual wind speed is difficult since little data is available relating the variation of wind speed with height above the water surface. Liss (1973) has measured the vertical profile of wind velocity at the downward end of a wind tunnel blowing over a water surface and observed that wind profiles

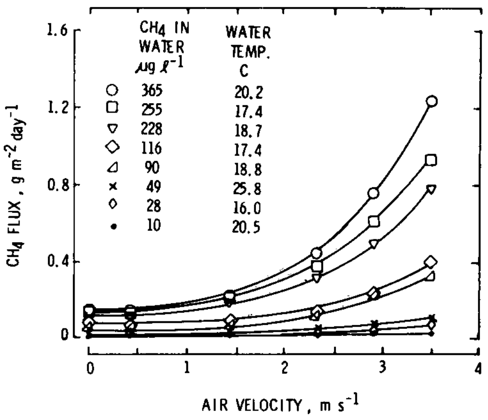

Fig. 2. Measured CH_4 flux as a function of air velocity and surface water dissolved CH_4 concentration. Surface water temperatures are also tabulated.

follow a logarithmic character of log z (height) versus wind speed. By using this relationship, it was found that the velocity measured at 2 cm above the water surface would be approximately 0.6 that at 1 meter and 0.5 that at 10 meters above the surface assuming that the extrapolation is valid. The primary limitation of this CH_4 monitoring system is that the wind–wave conditions generated in the chamber cannot be assumed to simulate each natural environment studied. However, for measurements in tidal creeks, forest-covered ponds and complex wet prairies, there are no practical alternative techniques to demonstrate the effects of wind speed.

5.2. *Flux measurements versus methane gradient across the interface*

Measured CH_4 flux, corrected to 20 °C water temperature, are plotted as a function of CH_4 concentration across the air–water interface in Fig. 3. Six sets of data are presented for air velocities ranging from 0 to 3.5 m s^{-1}. The liquid-phase exchange coefficient (k_l) of eq. (2) was evaluated for each of these data sets and is shown in each plot

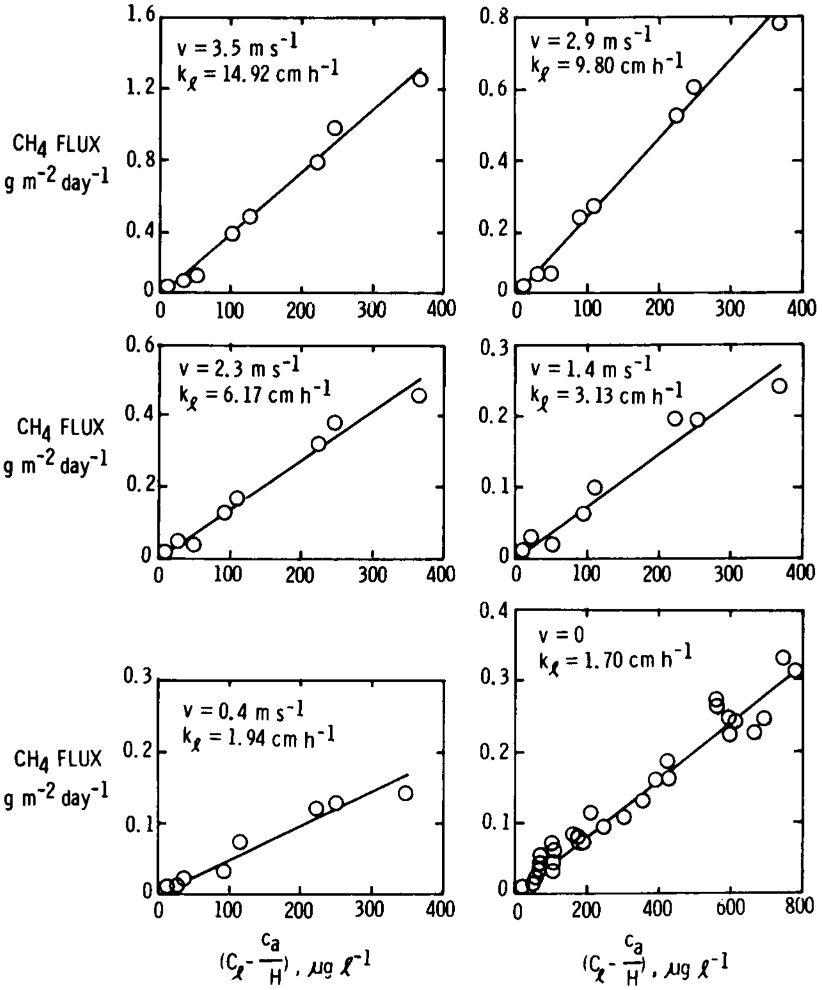

Fig. 3. Measured CH_4 flux versus CH_4 concentration difference across the air–water interface for air velocities (v) from 0 to 3.5 m s^{-1}. Air velocity was measured at 2 cm above the water surface. The CH_4 liquid phase exchange coefficients k_l corrected to a water temperature of 20 °C were evaluated using eq. (2).

along with the air velocity measured at 2 cm above the water. Seasonal temperature variations occurring during the time of this experiment resulted in surface water temperature variations from 12.2 °C to 29.0 °C for the $v = 0$ data set and 16.0 °C to 25.8 °C for the $v > 0$ data sets. Temperature corrections by the $(\mathrm{Sc}_{20}/\mathrm{Sc}_T)^{-2/3}$ factor ranged from 1.33 at 12.2 °C to 0.75 at 29.0 °C, but most of the data were collected at water temperatures near 20 °C where the correction factor was near unity.

5.3. *Liquid phase exchange coefficient*

Values of CH_4 liquid phase exchange coefficient (k_l), corrected to 20 °C water temperature, for the two-layer (film) model (eq. 2) evaluated above are plotted as a function of air velocity in Fig. 4. Surface water ripple heights, measured on a scale placed under the chamber and emerging through the interface, are also plotted in Fig. 4. There is an increasing rate of change in the initial exchange coefficient of 1.70 cm h^{-1} but no measurable change in the surface roughness until the air velocity exceeds about 1.4 m s^{-1}. Above this air velocity, the exchange coefficient exhibits a logarithmic characteristic and the water surface ripple height increases to approximately 3 mm at an air velocity of 3.5 m s^{-1}. The CH_4 liquid phase exchange coefficient was evaluated from Fig. 4 as

$$k_l = 1.70\ \mathrm{cm\ h^{-1}} \quad (v = 0)$$

and

$$k_l = 1.1 + 1.2v^{1.96}\ \mathrm{cm\ h^{-1}} \quad (v = 1.4 \text{ to } 3.5\ \mathrm{m\ s^{-1}})$$

At low velocities there are minimal wind effects until a critical velocity is reached. At that air velocity, shear effects are triggered, the water surface begins to ripple and the liquid phase exchange coefficient increases approximately as the square of the velocity. The critical air velocity of this experiment is lower than those observed in the other studies cited, probably due to the higher levels of dissolved CH_4 present in marsh waters and the higher sensitivity of the instruments used in this experiment. The CH_4 liquid phase exchange coefficient varied from 1.7 cm h^{-1} at $v = 0$ to 14.92 cm h^{-1} at $v = 3.5$ m s^{-1}. These values compare favorably with those measured for other gases such as O_2 and CO_2 (Downing and Truesdale, 1955; Kanwisher, 1963; Hoover and Berkshire, 1969; Liss, 1973).

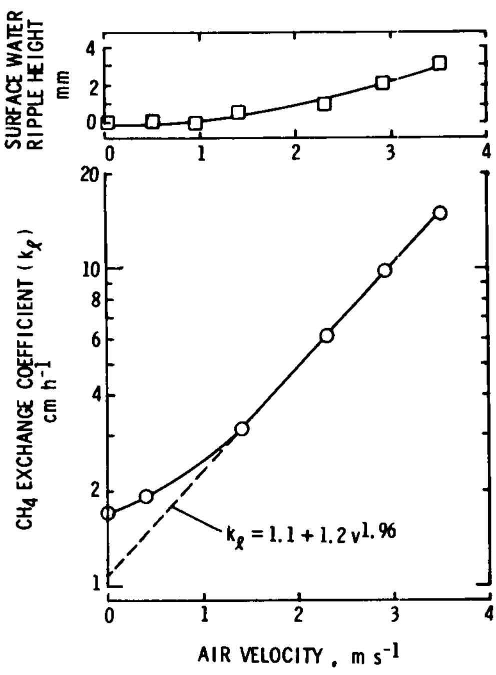

Fig. 4. CH_4 liquid phase exchange coefficient k_l at $T_w = 20$ °C and surface water ripple height versus air velocity measured at 2 cm above the air–water interface.

5.4. *Surface water depletion and circulation effects*

To evaluate the quality of these measurements, the effects of CH_4 depletion of the surface water and frictionally driven circulation produced by the chamber must be considered. Depletion would result in a loss of dissolved CH_4 and frictional circulation would result in a gain of surface water dissolved CH_4 if shallow stratification layers occurred over the CH_4 enriched bottom sediment. A sample calculation of CH_4 depletion for the highest flux measurement shown in Fig. 2 indicates that for a typical measurement time of 5 min the surface water will be depleted by 1.22 g m^{-2} day^{-1} or 0.004 g m^{-2}. The surface water contains 365 μg l^{-1} or 0.365 g m^{-3}. Since the water depth ranged between 0.5 to 1 m, we will assume a conservative effected water depth of 0.1 m which limits the surface water to 0.0365 g m^{-2} for depletion effects. The 0.004 g m^{-2} removed by the chamber amounts to a 10% depletion over the 5 min sampling time. Since CH_4 continues to diffuse upward from the bottom at the $v = 0$ rate or greater, the net loss will be less although a 10% error is considered reasonable. The key to success for these measurements results from the relatively short sampling time (5 min or less). To account for changes in the surface water dissolved CH_4 concentration due to depletion and for water stratification effects, water samples were taken before and after the sampling period. When CH_4 concentration changes greater than 10% were observed, the data was not utilized.

6. Concluding remarks

Methane loss to the atmosphere from flooded wetlands is influenced by the degree of supersaturation and wind stress at the water surface. Measurements in freshwater ponds in the St. Marks Wildlife Refuge, Florida, demonstrated that for the combined variability of CH_4 concentrations in surface water (10 to 780 μg l^{-1}) and air velocity over the water surface (0 to 3.5 m s^{-1}), CH_4 flux varied from 0.01 to 1.22 g m^{-2} day^{-1}. During periods of high water many wetlands of the world have significant areas of exposed, vegetation-free water surface which will be a highly variable source of methane to the atmosphere.

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